PRACTICAL CHEMISTRY

OR

QUALITATIVE CHEMICAL ANALYSIS

BY THE LATE

W. G. VALENTIN, F.C.S.

EDITED AND REVISED BY

W. R. HODGKINSON

FORMERLY SENIOR DEMONSTRATOR AND LECTURER IN THE NORMAL SCHOOL OF SCIENCE AND ROYAL SCHOOL OF MINES (NOW ROYAL COLLEGE OF SCIENCE); PROFESSOR OF CHEMISTRY AND PHYSICS IN THE ROYAL MILITARY ACADEMY AND ARTILLERY COLLEGE, WOOLWICH

JODRELL SCHOLAR, PH.D., F.R.S.E., F.I.C., F.C.S., F.G.S., ETC.

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MAP OF SPECTRA
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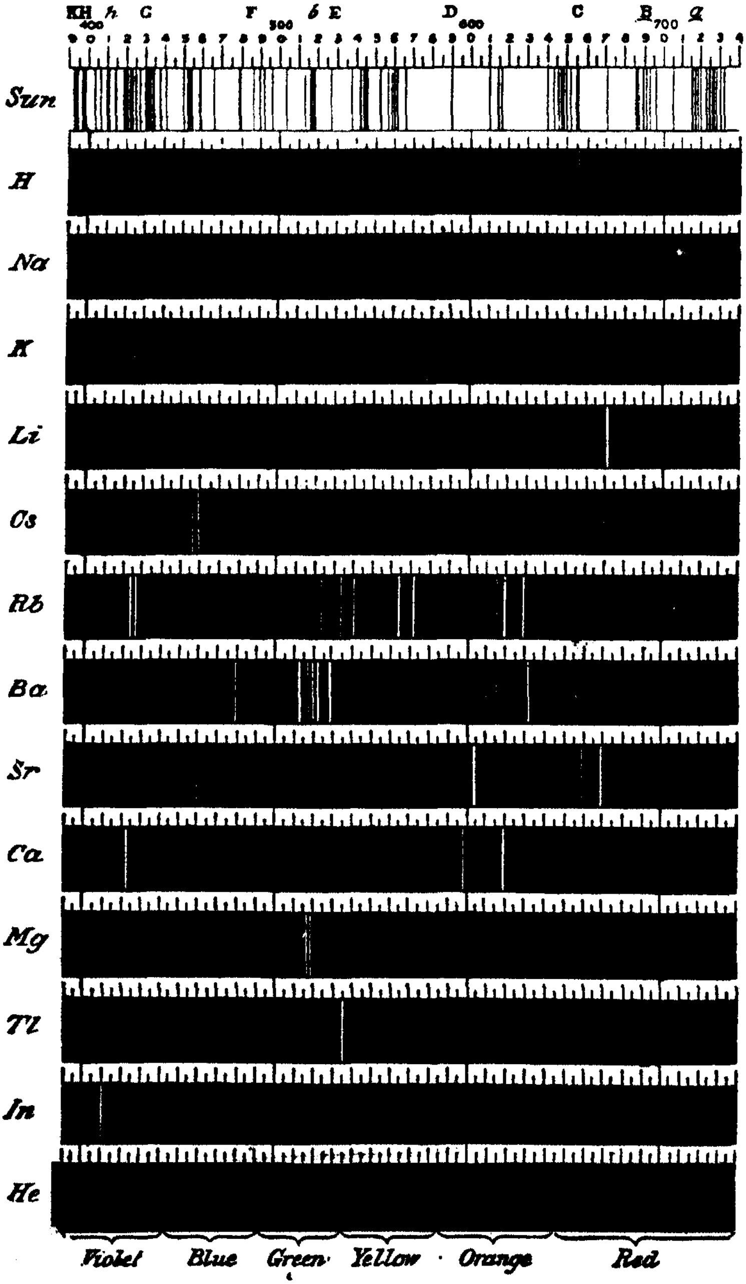

PREFACE TO THE NINTH EDITION.

THE plan of the work remains as in previous editions. Some alterations and additions, suggested by use, have been introduced, especially an extra chapter in which simple quantitative, including volumetric, operations are dealt with.

WOOLWICH,
June 1898.

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A COURSE

OF

PRACTICAL CHEMISTRY.

CHAPTER I.

INTRODUCTION.

DEFINITION OF QUALITATIVE ANALYSIS.—REAGENTS.—CHEMICAL OPERATIONS.

THE practical object of chemical analysis is to discover the presence or prove the absence of some particular elementary body or bodies in any given and unknown substance. To this end experiments are performed on the substance—questions are put to it—and from the result of these experiments, or the answers to the questions, the nature of the substance or substances is deduced. In addition to this, the performance of the operations in analysis has a great value as a means of training the observing and reasoning faculties, even when the practical results are not actually required. Before this can be fully recognised and applied it is, however, necessary to have a little knowledge of the properties or qualities of the chemical substances as regards each other. The properties of the so-called chemical elements must be first studied to some extent. These properties are, as far as is known, absolutely fixed and intrinsic within certain limits and conditions of experiment. Starting with this idea of fixity of quality, the methods of distinguishing and separating the elements or groups of elements in a complex substance will be found, as an exercise of the thinking faculties of the student, little inferior to mathematical methods.

The chemical student must strive to be as exact, cleanly, and methodical as possible in the performance of all the operations required.

Chemical actions, unlike some so-called physical, only take place on actual contact of the substances concerned.

Farther, there is no such thing as "nearly," either a chemical action takes place or it does not; very often, however, an action

commences but slowly, and may take some time before being completed.

And it also often happens that an action will run on several lines almost simultaneously. That is, there is often a secondary reaction starts just after a primary one, and then the two run on together.

Heating generally hastens or accelerates a reaction without further effect excepting a very high temperature be employed.

This is the rule. It is very seldom that a chemical action is as simple as $H_2 + Cl_2 = 2HCl$. Very frequently what is known as a see-saw series of reactions takes place, a substance being formed and decomposed and reformed within some narrow limits of temperature.

Reagents are substances employed as means of producing chemical changes. Reagents act upon and bring about changes in the substances under examination. They are usually divided, without any strict line of demarcation, into two classes—viz., general and special reagents. General reagents are those which separate a number of substances—groups in fact—at one operation; and special reagents those which are used to a limited extent only, and for the detection of individual substances.

Reagents may be gases, liquids, or solids, and either elements or compounds. In fact, if any two substances act on each other in such a manner as to produce a visible or permanent change, they are reagents to each other. Generally, however, the term applies to a known substance which is caused to act or is put into a position to act on an unknown one. The mode of application of a reagent depends on its nature and state. Gases require most apparatus. They are brought together in tubes with one open end dipping in mercury or water. Gases may be passed through liquids in bubbles, and solids may be heated, or not, in a stream of a gas in convenient tubes. Solids and solids require to be mixed most intimately or heated together, sometimes until one or both melt. Liquids on liquids or on solids are most easy to carry out. Almost any kind of containing vessel will do if it be so that the reaction can be observed. By liquids one understands solution in water generally.

A list of reagents, as well as directions for their preparation, will be found in an Appendix. Students who have not the advantage of working in a well-appointed laboratory, will need to devote some attention and care to the preparation of reagents.*

When two clear solutions of substances are brought in contact and a cloudiness results, a **precipitate** is said to be produced. It is in all cases owing to the formation of a new salt or substance, less soluble than the original substances. This is one of the most commonly employed operations in analysis, and is also the easiest to carry out.

Two gases in contact will also sometimes produce a solid. Frequently a solid is acted upon by a liquid or gas, so as to change in

* In the case of a large laboratory too much attention cannot be given to this, and the plan of normal or fractions of normal solutions is most strongly recommended.

colour or shape. Changes in form and colour are constantly made use of for the recognition of substances. Colour change is often the only visible evidence of a chemical action, and such colour tests are amongst the most delicate known.

FIG. 1.

Chemical Operations.—A reagent is added to a solution of an unknown body either by pouring it directly from the bottle or by running it from a pipette, as shown in Fig. 1. Sometimes a precipitation is produced by voltaic action, sometimes merely by the substitution of one solvent for another. One or more bodies may be precipitated by one and the same reagent. As most precipitates are heavier than the liquid in which they are formed, they fall to the bottom with more or less rapidity; and the supernatant liquid may often be poured off or **decanted**, without much disturbing the precipitate. This mode of separating fluids from precipitates is by far the most expeditious, and should be resorted to whenever it is applicable.* The precipitate may be washed in the vessel itself by treatment with hot water and repeated decantation.

When a large quantity of a fluid has to be removed from a precipitate, it is best to siphon off the overlying fluid. The precipitate may be washed with water, and the wash-water siphoned off repeatedly.

Filtration.—Small quantities of a precipitate which do not subside readily are more quickly separated by filtration. For this purpose

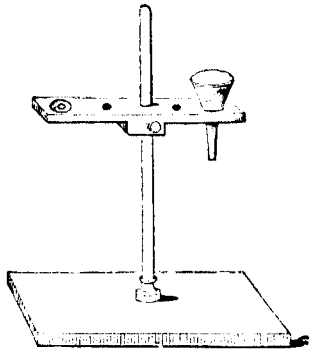


FIG. 2.

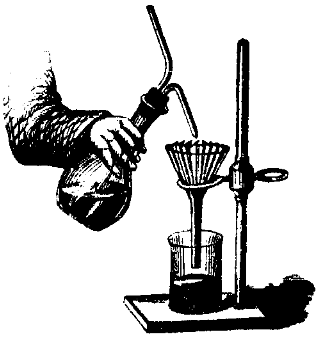


FIG. 3.

funnels are used, mostly of glass, conical in shape, and inclined at an angle of 60°. They may be conveniently supported on a wooden stand, Fig. 2, or an iron or brass filtering stand as Fig. 3. The

* It will be noted, however, that *some* of the substance must be lost by this treatment, so that it can only be resorted to when the materials are in plenty.

filtering paper should be porous and unsized, and cut in the form of a round sheet, which by being folded twice in the shape of a quadrant, forms, on opening up, a paper cone, at an angle of 60°. Plaited filters allow the liquid to pass more rapidly through them, as a greater surface of one-thickness paper is exposed. The filter should exactly fit the funnel, without reaching quite to the rim, and should be moistened in the funnel with distilled water before any solution is poured through it. As most kinds of filtering paper contain traces of iron, lime, silica, &c., acid liquids frequently dissolve out traces of these bodies. In all accurate analyses the filtering paper should, on this account, be washed first with dilute hydrochloric or nitric acid, and then with hot water, before being used.

Washing.—Most precipitates retain with great pertinacity traces of the fluid in which they were suspended, and it is therefore of the utmost importance to thoroughly wash them in order to obtain accurate results. For this purpose a wash-bottle (Fig. 3) is employed, whereby a fine jet of hot, or cold, distilled water can be directed on to the filter in such a manner as to loosen and detach the precipitate from the paper and percolate thoroughly. The liquid should at no time quite fill the filter, as some precipitates have a tendency to creep up and to get between the paper and the glass, and are carried into the filtrate. This would entail repeated filtration. The washing of a precipitate on the filter is affected most rapidly by allowing the wash-water to run off entirely each time before adding fresh quantities of distilled water. By repeating this four or five times, most precipitates will be found sufficiently washed for *qualitative* purposes.

The student must especially guard himself against using too large a quantity of the substance he wishes to examine.* Bulky or voluminous precipitates entail much washing, an operation which is tedious but *must* be done well.

Test-tubes are the vessels used for the operations of precipitation and separation in qualitative analysis, especially as there is generally no need for collecting the wash-water or adding it to the main filtrate. These tubes are conveniently placed in a test-tube stand (Fig. 4). After being well cleansed by the aid of a test-tube brush, and rinsed out with distilled water, they should be set aside to drain in a basket or rack.

Small flasks or beakers are sometimes employed if an analysis involves the separation of a small quantity of one substance from a large amount of another, and when, of necessity, large quantities of the substance must be operated upon, but are not advised for ordinary work.

Porcelain dishes are employed for the purposes of concentration, evaporation, or ignition. They can be heated either by means of

* Even in a *qualitative* analysis it is an excellent thing to have an idea of the weight of substance taken. In the earlier experiments it is advised to weigh out, roughly, from ·5 to 2 grms. of the substance. Also to dissolve in a known amount of water and to employ normal solutions of reagents. (See Appendix.)

a spirit lamp, or by means of a Bunsen gas lamp, provided with a rose top. Sometimes a sheet of iron wire gauze or a sand-bath or asbestos cloth or card is interposed between the porcelain vessels and the gas flame, and is supported on a retort stand ring or tripod stand.

If solid substances have to be examined, they should always be powdered in a mortar—an agate mortar should be employed for

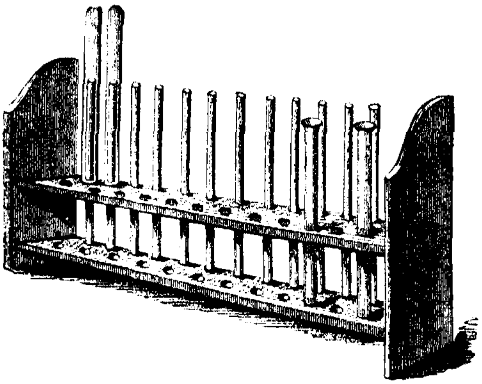


FIG. 4.

hard substances, *e.g.*, most minerals—before being acted upon by water, acids, &c.

When very small quantities of a substance are at disposal, or when valuable reagents are employed, watch glasses or porcelain crucibles may be used instead of test-tubes, &c.

For the ignition of precipitates porcelain crucibles or small porcelain dishes are used, and in some cases, where no injury can arise, platinum capsules or cups made of platinum foil, such as may be made by folding up platinum foil into a cone or filter shape.

One object of qualitative analysis is (1) to recognise or detect elementary and compound substances contained in an unknown mixture; (2) to separate elements or groups from each other. These are practical objects. It has also an equal value as a means of inculcating quick and accurate observation. The performance of exercises in qualitative analysis is to some extent like a game of chess with many more pieces, and when properly conducted develops and strengthens the observing and reasoning faculties of the student in an eminent degree.

CLASSIFICATION OF REAGENTS.

There are certain reagents which effect the simultaneous separation of a number of bodies contained in a common solution, leaving others in solution. Such general reagents are called group-reagents.

To appreciate their general effect perform this or some similar exercise:

Mix and dissolve in water small quantities of the nitrates of the following metals:—Silver, copper, cobalt, barium, potassium, and to the mixed solution add—

I. Hydrochloric acid, a white curdy precipitate is obtained, consisting of silver chloride, AgCl; filter. To the filtrate add—

II. Sulphuretted hydrogen, a black precipitate is obtained consisting of cupric sulphide, CuS; filter again, and to the filtrate add—

III. {Ammonium chloride, Ammonia and Ammonium sulphide} A black precipitate is formed consisting of cobaltous sulphide, CoS; filter, and to the filtrate add—

IV. Ammonium carbonate, a white precipitate is obtained, consisting of barium carbonate, $BaCO_3$; filter, evaporate the filtrate and heat to redness to drive off the ammonium salts. A white saline residue is left, containing the potassium salt.

These changes are evidently produced by the mutual exchange of elements between two bodies (changes by double decomposition): *i.e.*, the hydrochloric acid added in Group I. to the solution of the metallic nitrates, exchanges its hydrogen for the silver of the silver nitrate: and the sulphuretted hydrogen exchanges its hydrogen for the metal copper, leaving nitric acid and cupric sulphide, &c.

These reactions as expressed by equations, are—

$AgNO_3$ Silver nitrate.	+	HCl	=	$AgCl$ Silver chloride	+	HNO_3.
$Cu(NO_3)_2$ Cupric nitrate.	+	SH_2	=	CuS Cupric sulphide.	+	$2HNO_3$.
$Co(NO_3)_2$ Cobaltous nitrate.	+	$S(NH_4)_2$	=	CoS Cobaltous sulphide.	+	$2NH_4NO_3$.
$Ba(NO_3)_2$ Barium nitrate.	+	$(NH_4)_2CO_3$	=	$BaCO_3$ Barium carbonate.	+	$2NH_4NO_3$.

These are, however, not the only metals which may be separated by the same reagents.

The table on the next page exhibits five groups into which the most commonly occurring metallic elements may be classified by the action of the several group-reagents.

Thus far group-reagents assist in the separation of bodies, but when, as in Group IV., the white precipitate produced by the group-reagent, ammonium carbonate, leaves still a doubt whether a barium, strontium, or calcium compound was present in the solution, further experiments must evidently be made with a view of completely identifying the substance under examination. This the student will only be able to do by making himself first *practically familiar with*

ANALYTICAL CLASSIFICATION OF THE METALS,

WITH THEIR RESPECTIVE GROUP-REAGENTS.

GROUP I. Iydrochloric Acid.	GROUP II. Sulphuretted hydrogen, in acid solutions. N.B.—Nitric acid should be absent.	GROUP III. Ammonium Chloride, Ammonia, and Ammonium Sulphide.	GROUP IV. Ammonium Chloride, Ammonia, and Ammonium Carbonate	GROUP V. (No characteristic group-reagent.)
ead . as $PbCl_2$.*	Mercury . . . as HgS, black.	(1) *Hydrates.*	Barium as $BaCO_3$	*In solution:*
lver . ,, AgCl.	Lead . . . . ,, PbS,‡ ,,	Aluminium as $Al_2(HO_6)$, white.	Strontium ,, $SrCO_3$	Magnesium.
ercury ,, Hg_2Cl_2.†	Bismuth . . . ,, Bi_2S_3, ,,	Chromium ,, $Cr_2(HO_6)$, green.	Calcium ,, $CaCO_3$	Potassium.
	Copper . . . ,, CuS, ,,			Sodium.
	Cadmium . . ,, CdS, yellow.	(2) *Sulphides.*		Ammonium.
	Tin (Stannosum) ,, SnS, brown.	Iron . . . as FeS, black.		
	Tin (Stannicum) ,, SnS_2, yellow.	Zinc . . . ,, ZnS, white.		
	Antimony . . ,, Sb_2S_3, orange.	Manganese ,, MnS, buff.§		
	Arsenic . . . ,, As_2S_3, yellow.	Nickel . . ,, NiS, black.		
	Gold . . . . ,, Au_2S_3, black.	Cobalt . . ,, CoS, ,,		
	Platinum . . ,, PtS_2, ,,			
		(3) Phosphates, Arsenates, Borates, Silicates, Fluorides, &c., of metals other than the alkalies.		

* When no colour is stated, the precipitate is white. There are degrees of whiteness, however, depending on the physical condition, density, crystalline form, &c., of the precipitate.

† Precipitated as mercurous chloride from mercurous salts.

‡ Lead chloride, $PbCl_2$, being somewhat soluble even in cold water, lead is found both in the first and second group.

§ Varies in colour somewhat depending on concentration and temperature of solutions.

N.B.—Most of the so-called rare metals can be "placed" in these groups, but are omitted here for simplicity.

the different changes or reactions which the members of the various groups of metals can be made to undergo ; and after understanding the use of the group-reagents, he should direct his attention to the special reactions which distinguish and separate one metal from another, or from several others. This may frequently be done in more than one way; one reaction, however, sometimes deserves the preference over others, on account of the greater exactness which distinguishes it, or on account of increased facility of execution, or of both.

Certain reactions, lastly, will have to be studied, which are not directly available for the separation of the members of a group from each other, but to which considerable interest is attached as being illustrative of some valuable property or other of the metals.

The tabular form as the most compact and summary mode of arranging chemical reactions will often be adopted for embodying such reliable and expeditious methods of separation as have stood the test of experience in the laboratory. The directions given will be concise and divested of all explanatory matter. *On no account should a student use any tabular directions, however, without first having made himself practically acquainted with the details of the reactions ;* and to counteract any pernicious influence which the use of tables might have, the student should exercise and learn to draw up tables for the several other processes of separation which are frequently possible.

In previous editions of this work, several methods of writing the chemical formulæ of bodies were employed. This it was found had a tendency to confuse the beginner, as the identity of a substance which was written in different ways was not always immediately obvious. In the present edition it has been thought better not to attempt to give, or at any rate introduce into the text, any constitutional formula for inorganic compounds ; but, in the case of organic substances where there is no doubt as to the relative arrangement of the atoms in their molecules, full constitutional formulæ are employed.

An appendix will be found to contain alternative, in some cases structural, formulæ for some characteristic mineral compounds.

When a metal enters into combination with another substance it loses some of its individuality. To some extent the new compound acts as an independent individual, its characters being influenced to a greater or less degree by those of its constituent elements. One of these elements in a compound usually imparts its character in a dominant degree, as in the case of the metallic compounds termed salts, from which we get the reactions of the metals in combination.

The combining or equivalent values, or atomicities of the elements, are indicated by the use of dashes and Roman numerals placed above the symbols of the elements, thus :—H' Zn'', Au''', C^{iv}, N^{v}. S^{vi}.

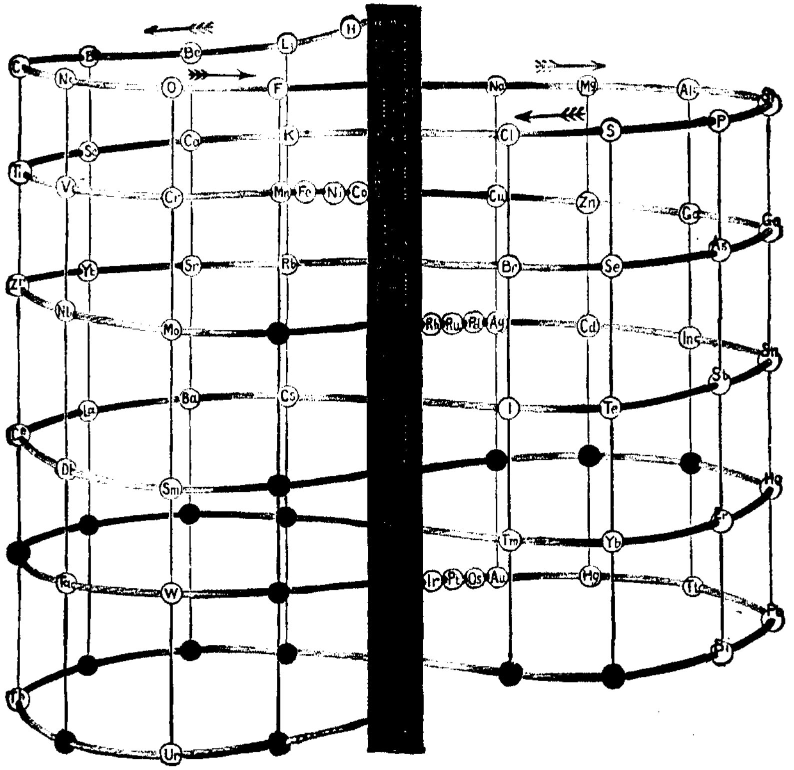
These combining values or atomicity marks do not at all indicate the intensity of chemical attraction or energy of union, but merely the extent or quantity of attraction of one element for another

Name.	Symbol of the Atom and Valency Marks.	Atomic Weights. Commonly used.	Loth, Meyer, and Seubert. O = 1.	H = 1.	Specific Heats.
Hydrogen (Normal element)	H	1	0·06265	1	(2·3)
Aluminium	Al‴, iv	27·5	1·694	27·04	0·2143
Antimony	Sb‴, v	122	7·494	119·6	0·0508
Argon					
Arsenic	As‴, v	75	4·693	74·9	0·0814
Barium	Ba″	137	8·575	136·86	(0·047)
Beryllium	Be″, or ‴	9·4	0·569	9·08	0·4079
Bismuth	Bi‴, v	210	13·00	207·5	0·0308
Boron	B‴, v	11	0·683	10·9	0·366 at 233°
Bromine	Br′, ‴, v, vii	80	4·997	79·76	3·0843 (solid)
Cadmium	Cd″	112	7·00	111·7	0·0567
Cæsium	Cs′	133	8·315	132·7	
Calcium	Ca″	40	2·501	39·91	0·167
Cerium	Ce″, vi	138	8·847	114·2	0·0448
Chlorine	Cl′, ‴, v, vii	35·5	2·2159	35·37	(0·18)
Chromium	Criv, vi,	52·5	3·284	52·45	0·100
Cobalt	Co″, iv	59	3·67	58·6	0·1076
Carbon	C″, iv	12	0·7502	11·97	0·459 at 985°
Copper	Cu″	63	3·959	63·18	0·0952
Didymium	Diiv	145	9·09	145·0	0·0456
Erbium	Er″	169	10·40	166	
Fluorine	F′	19	1·194	19·06	(3·26)
Gallium	Gaiv	69	4·38	69·9	0·079 (solid)
Gold	Au′, ‴	196·7	12·29	196·2	0·0324
Germanium	Geiv	72·32			0·0758
Helium					
Hydrogen	H′	1	0·06265	1·00	(2·3)
Indium	In‴	113·4	7·108	113·4	0·0569
Iridium	Ir″, iv, vi	193	12·06	192·5	0·0326
Iodine	I‴ v, vii	127	7·9284	126·54	0·0541
Iron	Fe″, iv, vi	56	3·501	55·88	0·1138
Lanthanum	Laiv	139	8·680	138·5	0·0449
Lead	Pb″, iv	207	12·932	206·39	0·0314
Lithium	Li′	7	0·439	7·01	0·9408
Magnesium	Mg″	24	1.500	23·94	0·2499
Manganese	Mn″, iv, vi, viii	55	3·43	54·8	0·1217
Molybdenum	Movi	96	6·01	95·9	0·0722
Mercury	Hg″	200	12·52	199·8	0·0319
Nitrogen	N‴, v	14	0·8779	14·01	(0·36)
Nickel	Ni″, iv	58·8	3·67	58·6	0·1082
Niobium	Nbv	94	5·87	93·7	
Osmium	Os″, iv, vi, viii	199	2·2	195	0·0311
Oxygen	O″	16	1·00	15·96	(0·25)
Palladium	Pd″, iv, vi	106·5	6·66	106·2	0·0593
Phosphorus	P‴, v	31	1·940	30·96	0·1895
Platinum	Pt″, iv, vi	197·18	12·177	194·34	0·0324
Potassium	K′	39	2·443	39·03	0·1655
Rhodium	Rh″, iv, vi	104	6·51	104·1	0·0580
Rubidium	Rb′	85	5·34	85·2	(0·077)
Ruthenium	Ru″, iv, vi, viii	104	6·49	103·5	0·0611
Scandium	Sc	44	2·755	43·97	
Sulphur	S″, iv, vi	32	2·0037	31·98	0·1776
Selenium	Se″, iv, vi	79	4·942	78·87	0·0762
Silver	Ag′	108	6·7456	107·66	0·0569
Silicon	Siiv	28	1·754	28·0	0·203 at 232°
Sodium	Na′	23	1·4408	22·995	0·2934
Strontium	Sr″	87·5	5·47	87·3	(0·074)
Tantalum	Tav	182	1·42	182	
Tellurium	Te″, iv, vi	128	18·00	127·7	0·0474
Thallium	Tl′, ‴	204	12·76	203·7	0·0336
Thorium	Thiv	231·5	14·534	231·96	
Titanium	Tiiv	50	3·15	50·25	(0·13)
Tin	Sniv	118	7·353	117·35	0·0562
Uranium	Uiv, vi	240	15·03	239·8	0·0276
Vanadium	V‴, v	51·2	3·20	51·1	
Wolfram	Wiv	184	11·50	183·6	0·0334
Ytterbium	Yt	89	10·81	172·6	
Yttrium	Yiv	93	5·61	89·6	
Zinc	Zn″	65	4·065	64·88	0·0955
Zirconium	Zriv	90	5·66	90·4	0·0662

NEWLAND'S AND MENDELEEFF'S TABLE OF THE ELEMENTS ARRANGED AS A PERIODIC SERIES.

Series.	Group I. R_2O.	Group II. RO.	Group III. R_2O_3.	Group IV. RH_4 RO_2.	Group V. RH_3 R_2O_5.	Group VI. RH_2 RO_3.	Group VII. RH R_2O_7.	Group VIII. RO_4.
1	H=1							
2	Li=7	Be=9·0	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5	
4	K=39	Ca=40	Sc=44	Ti=50	V=51	Cr=52	Mn=55	Fe=56, Co=59 Ni=58, Cu=63
5	(Cu=63)	Zn=65	Ga=69	Ge=72	As=75	Se=79	Br=80	
6	Rb=85	Sr=87	Yt=89	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104 Pd=106, Ag=108
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	I=127	
8	Cs=133	Ba=137	La=138	Ce=140	—	Di=145	—	— —
9	(—)	—	—	—	—	—	—	
10	—165	— 169	Er=170	YB=172·6	Ta=182	W=184	—	Pt=194, Os=195(?) Ir=192, Au=196
11	(Au=196)	Hg=200	Tl=204	Pb=206	Bi=210	—	—	
12	—	—	—	Th=231	—	U=238	—	— —

CROOKES' LEMNISCATE DIAGRAM OF SYNTHESIS OF ELEMENTS.



expressed in terms of hydrogen as the unit. They also are not always constant.

Up to the present date the elements as in the list on p. 9 have been isolated and recognised.*

A deviation from the apparently more natural course of studying the reactions of the metals by beginning with Group I., and so on, is thought to be justified on the ground of the comparative simplicity of the metals of Group V., especially the alkali metals. Experience has shown that students have less difficulty in mastering the reactions by reversing the actual working order of the groups, beginning with the study of the alkali and alkaline-earthy metals; and that a thorough knowledge of the metals of these groups is of material assistance in understanding the qualitative changes to which the heavier metals are subjected.

Previous to commencing the actual testing for metals, acids, &c. in minerals or salts, or even in a prepared solution of the group, it is highly recommended to the student to perform some at least of the following experiments:

The order of experiment is:

I. Action of oxygen (air). A small piece of the element is placed in the bent tube, which is then heated so that a current of air can pass over the substance.

Many substances combine with oxygen under these circumstances, and in most cases ash-like solids are produced called oxides.

These oxides have sometimes characteristic colours; some are soluble in water, some volatile, and other properties which distinguish them.

II. The action of water. Some substances act upon cold water, others require to be heated in steam.

III. Action of sulphur. For this the substance is simply heated or melted with sulphur in a dry test tube.

IV. Action of acids, as sulphuric, nitric, hydrochloric or alkalies, as soda or ammonia.

These may also be done either in a test tube, or better in a small dish, so that the product may be obtained in a dry state by evaporating off the water and excess of acids employed. Salts may be obtained in this way, and then used for the *analytical testing*.

* The diagrams on pages 10 and 11 are intended to exhibit the genetic relations of the elements to each other as derived from their atomic weights and general chemical characters.

Both attempt to show the periodic recurrence of similar functions or properties, and the probable existence of "triads" or groups of several elements whose properties and general behaviour are very similar. The elegant diagram on p. 11 is intended to picture the probable condensation, due to cooling and motion in space, of an original molecule. (See Crookes' presidential address, Chemical Society, 1888.)

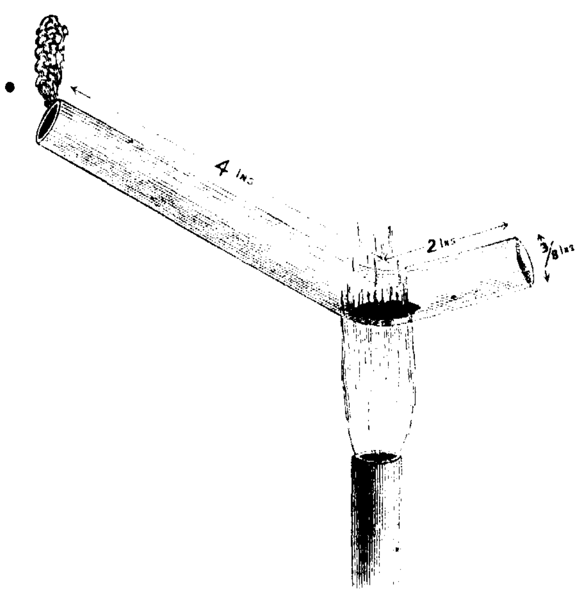


Fig. 5.

CHAPTER II.

REACTIONS OF THE METALS OF GROUP V.

This group comprises the metals potassium, sodium, ammonium, and magnesium, which are not precipitated by any group-reagent, as most of their compounds are very soluble in water.

1. **POTASSIUM**, K. Atomic weight, 39·1. Specific gravity, 0·87. Melting point, 62·5° C. Boiling point, 719–731° C. — Is found in combination in large amount only in a few minerals, of which saltpetre is the most important. It is present in larger or smaller quantities in a few silicates and sulphates, such as felspar. In the ashes of plants (crude potashes), and in the form of chloride in saline deposits (at Stassfurth in Germany and elsewhere).

The metal is obtained by driving the hydrate over very strongly heated iron turnings. It has a brilliant silver-white lustre on a freshly cut surface, which immediately tarnishes on contact with air, becoming covered with oxide. It decomposes water when brought in contact with it, the heat produced being sufficient to inflame the liberated hydrogen. The metal is so soft that it may be squeezed easily by gently pressing a small piece with the end of a test tube or glass rod. It is generally kept under rock oil or paraffin, to prevent oxidation.

EXPERIMENTS.

I. A very small piece, not larger than a pea, of the metal is taken from the petroleum, dried between several thicknesses of dry blotting-paper and introduced into the tube. (Fig. 5.)

The tube is held in tongs over the Bunsen flame. The metal will melt and then ignite in the current of air. White fumes will escape at the upper end of tube, and a greyish substance, mostly K_2O, will form and partly sublime up the tube. Allow to cool, then very carefully immerse one end of tube in a dish of cold water. The greyish oxide will dissolve and the temperature will rise considerably. Great care must be taken that all the metal has oxidised, or an explosion may result.

The water will be found to convert red litmus into blue. Reserve this solution.

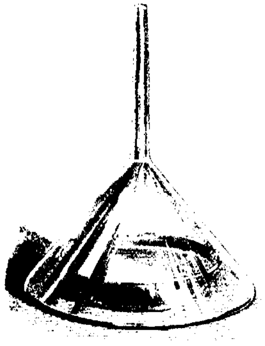


Fig. 6.

II. Carefully wipe as before a very small piece, less than in I., of the metal, and drop on to some perfectly clean and cold water contained in a dish covered by a funnel, as in Fig. 6.

A beaker covered by funnel will do as well. The metal will appear to burn. It is really hydrogen, but it is coloured by some potassium vapour. A red hot globule of potassium oxide swims on the water, and finally dissolves with a slight explosion.

Test this solution as in I. Then add a diluted acid drop by drop until litmus paper shows neither red nor blue, but a claret tint. A salt of potassium has been formed. Evaporate the solution to dryness, when crystals of the salt will be left.

III. Place a small quantity, ·5 grm., sulphur in a perfectly dry tube, drop into this a very small piece of potassium, hold tube in tongs, heat gently, combination takes place energetically. When cool the product is brown or black. It is K_2S or K_2S_n. Place in water carefully. It gives a yellow solution, which also turns red litmus blue. On neutralising by an acid as before, SH_2, sulphuretted hydrogen is given off, and some sulphur is generally precipitated.

N.B.—Do not touch the metal with the fingers or bring it in contact with acids.

DRY REACTIONS.*

Most potassium compounds when heated in small quantities on a thin platinum wire in the inner flame of the blowpipe, or in the lower outer edge of the Bunsen flame, undergo dissociation, the vapour of the metal imparting a violet colour to the outer flame. When examined with the aid of a spectroscope,† the potassium

* When solids are heated in a tube, or on charcoal, or on a platinum wire, without any liquid being employed on them, they are said to be undergoing "**dry**" *reactions*, or the *dry examination*.

These dry reactions are given, as a rule, by every compound of the element. When dissolved in water or other solvent, and this solution is treated with *reagents*, it is undergoing "**wet**" *tests*, or *reactions in solution*.

As regards wet reactions, almost any soluble compound of the element will answer. Some do so in an eminent degree, and are also easy to obtain. Nitrates, chlorides, sulphates, are, generally speaking, most useful, and should be used in doing the reactions. Oxides, sulphides, phosphides, and insoluble compounds *are less suitable, as they sometimes complicate matters for* beginners by producing secondary reactions or complex products.

N.B. Students are advised to perform all the test experiments with each metal of a group, and then attempt a method of separation founded on the knowledge gained. Use the salts you have made from the metal, if possible, for the first reactions.

† When elements in the gaseous condition, or vapourised by strong ignition, are examined by means of the spectroscope, they may be distinguished from each other by the respective spectra which they give. The intensity of the spectra of *metallic elements is so much greater than that of the non-metals,* that the latter are only rarely seen. The heat which can be produced by a good Bunsen gas burner is not strong enough to volatilise all elements or to heat their vapour highly enough. Most heavy metals can only be volatilised by means of an electric spark, making use of an induction coil, by placing the metals between the electrodes. In order to analyse the ordinary gases spectroscopically, the spark is passed through the gases, contained in tubes which are filled with the gas and then exhausted with an air-pump. The filling and exhausting is repeated several times, and finally a good vacuum obtained. Traces of the gases are left, which on agitation by an induction spark become luminous. These tubes can be made by any one if the use of a sprengel or other mercury pump is available. (See Fig. 7, page 16.)

It is usual to employ the spectroscope only for the examination of those elements which can be volatilised by means of a gas flame, a good Bunsen burner, such as the alkali metals, sodium, potassium, rubidium, cæsium, lithium; the alkaline earthy metals, barium, strontium, calcium; and

spectrum is found to consist mainly of two lines, a comparatively strong line, Kα,* in the red, and a faint line, Kβ,* in the blue.

This applies more particularly to potassium salts, which are volatile without decomposition at a strong red heat (such as potassium chloride, bromide, iodide, and cyanide) or which are decomposed by heat; but not to non-volatile potassium salts, such as phosphates, silicates, or borates, which give scarcely any flame reaction till they are moistened with an acid, as hydrochloric, or, if that be without action, heated together with pure calcium sulphate or silver sulphate. The presence of sodium compounds gives rise to an intense golden-yellow flame, which conceals the potassium reaction; but when seen through a blue glass, or indigo solution, the yellow or sodium flame is entirely cut off, and the potassium flame becomes distinctly visible, and is then of a rich reddish-violet colour.

A more simple method of detecting potassium in the presence of a large quantity of sodium compounds is the following:—A small portion of the substance is moistened with concentrated hydrochloric acid and placed on a loop of thin platinum wire. The wire is then gradually brought near to a point in the Bunsen flame, about half an inch above the top of the burner. Compounds of potassium being more volatile than those of sodium, the violet-coloured flame

the heavy metals, thallium and indium. Lead, copper, arsenic, antimony, and some other metals, and phosphorus, boric acid, and less easily sulphur, selenium, tellurium, will also show colours in a Bunsen flame, and a few lines

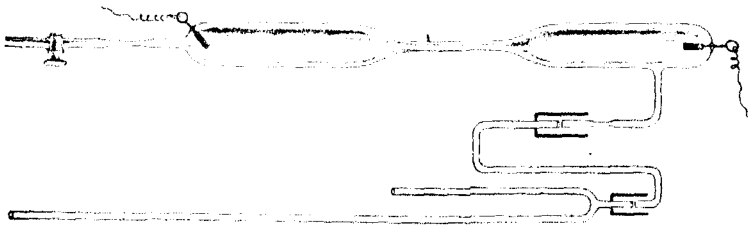


FIG. 7.

may be distinguished. The compounds most suitable are the chlorides, nitrates, chlorates, and carbonates of the metals. A small portion is placed on a loop of thin platinum wire, introduced into the non-luminous portion of the flame, and the spectrum examined. The different elements are distinguishable by their respective colours, as well as by the position which their lines occupy in the continuous solar spectrum. The lines are not all of the same intensity, and therefore not equally available.

It is only by employing large quantities of pure substances, and heating them very intensely, that many of the less prominent lines can be observed. The delicacy of the reaction is, however, so great that the merest traces can be discovered. Spectroscopic analysis constitutes a most valuable auxiliary to ordinary chemical analysis.

* Principal spectral lines of elements are generally designated by a letter for ordinary reference purposes. Compare the table of some metallic elements opposite title-page.

will be clearly observed before any trace of the yellow sodium flame is visible.

REACTIONS IN SOLUTION.

Nearly all potassium salts are soluble in water.

$PtCl_4$ (platinic chloride) precipitates from potassium solutions which are not very dilute, a yellow crystalline precipitate of potassium platinic chloride, $2KCl.PtCl_4$, insoluble * in strong alcohol, or better still in alcohol and ether, as well as in acids.

$C_2H_2(OH)_2(CO_2H)_2$ (tartaric acid) precipitates white crystalline hydrogen potassium tartrate, $C_2H_2(OH)_2CO_2HCO_2K$ from neutral and sufficiently concentrated solutions. The precipitate settles rapidly, especially after shaking or stirring.

$2HF,SiF_4$ (hydrofluosilicic acid) gives a white gelatinous precipitate of potassium silicofluoride, $2KF,SiF_4$; difficultly soluble in water (1 in 833 parts at 17·5° C.); insoluble in alcohol.

Potassium salts are for the most part soluble in water, hence so few precipitates. The hydrate and carbonate constitute two important reagents, on account of the great affinity which the powerful base potassium possesses for the acids with which the metals of other groups may be combined.

2. **SODIUM,** Na′. Atomic weight, 23. Specific gravity 0·974. Melting point, 96° C.—This metal somewhat resembles potassium in appearance, but is a little harder, and does not oxidise so rapidly in air, nor is its action on water so energetic as that of the latter metal. Its compounds occur in nature in vast masses, as rock salt, NaCl; as carbonate, in native soda, $Na_2CO_3,10OH_2$, and in trona, $Na_2CO_3,2HNaCO_3,3OH_2$; as nitrate, in cubic nitre, or Chili saltpetre, $NaNO_3$; as sulphate or Glauber's salt, $Na_2SO_4,10OH_2$; as biborate, $Na_2B_4O_7,10OH_2$; as glauberite, $Na_2SO_4,CaSO_4$; and as cryolite, $6NaF,Al_2F_6$; and in many silicates, of which albite may be taken as the representative. Nearly all sodium compounds are easily soluble in water, a few silicates and cryolite excepted.

Sodium may be obtained in a similar manner to potassium and also by heating the hydrate or oxide to a high temperature with carbon. The metal distils over similarly to potassium, and may be kept under petroleum or in a perfectly dry atmosphere.

EXPERIMENTS.

I. A small piece of sodium (freed from oil) heated in the tube behaves very like K, but requires a little higher temperature before burning. The oxide produced is generally whiter than with K. Its behaviour with water is almost identical with K.

II. A small piece of the metal placed in cold water, as with potassium, melts and runs about and disengages hydrogen, which may be set on fire. The flame is coloured intensely yellow. A globule of red hot oxide floats on

* The degree of solubility of a precipitate in different media can only be ascertained by laborious quantitative experiments. The student will therefore be expected to verify only those statements respecting the solubility of the precipitates which require no quantitative knowledge.

the water, and finally dissolves, spirting or exploding as it cools down. The solution is alkaline to litmus as with the potassium.

Neutralise the two solutions with an acid, and evaporate to dryness. Note in each case the physical characters of the salts produced, whether deliquescent, &c.

Sodium should not be touched by the fingers, and must not be put in contact with acids.

III. Gently warmed with sulphur in a dry tube the reaction is similar to that with K. The sodium sulphide also dissolves in water. The product is Na_2S or Na_2S_2 or a mixture of these.

DRY REACTIONS.

The intense golden-yellow colour which sodium compounds impart to the outer blowpipe flame is almost exclusively relied upon for the detection of the metal. Its spectrum consists of a bright double line, coinciding with the D line of the solar spectrum, and several green lines seldom seen. Some sodium salts are readily recognised by their characteristic taste, especially rock salt and cubic nitre.

REACTIONS IN SOLUTION.

Sodium salts are even more freely soluble than potassium salts, and platinic chloride or tartaric acid give no precipitates, although analogous compounds are formed. Hydrofluosilicic acid gives a gelatinous precipitate from concentrated (aqueous) solutions only; the precipitate is insoluble in alcohol.

Sodium hydrate and sodium carbonate act in many respects like potassium hydrate and carbonate.

3. **AMMONIUM,** NH_4, generally shortened to Am. Combining weight, 18. Hypothetical metal or "compound radicle" in combination.

Ammonia, NH_3, is obtainable from nitrates by the action of nascent hydrogen, as when moist iron or zinc filings or aluminium are mixed and heated with a nitrate; from the distillation of many organic compounds containing nitrogen with a hydrate as KHO. Its chief commercial source at present is coal, the NH_3 being formed during the heating of coal in the gas manufacture. From the coal-gas it is separated by washing with water and weak acids.

EXPERIMENTS.

Mix a few grams of potassium nitrate with five or six times as much fine iron filings and moisten very slightly. Warm the mixture gently in a test tube fitted with a cork and glass tube. (*See* Chlorine later.)

Catch some of the gas in an inverted dry test tube in which a piece of red litmus paper has been placed. Fill another tube similarly and then introduce a few drops of water, close tube with thumb and shake, a partial vacuum will be formed by the gas dissolving in the water. Add litmus to the water. Add acid to this water until neutral, and evaporate carefully to dryness, best on a water-bath; an ammonium salt is formed.

The reaction between nitrate and moist iron is probably

$$a \quad 2(KNO_3) + 5Fe = 5FeO + K_2O + N_2$$

and at the same time

$$\beta \quad 3Fe + 3H_2O = 3FeO + 6H.$$

The H and N being liberated together combine to form $2(NH_3)$. The reactions may be more complex than this.

Any ammonium compound, as sal ammoniac, NH_4Cl, when mixed and warmed with CaO, lime, or almost any other oxide or hydrate, will give off NH_3 as gas.

$$2NH_4Cl + CaO = 2NH_3 + H_2O + CaCl_2.$$

The gas is very soluble in cold water but may be expelled on boiling for a short time.

Alcohol dissolves still more NH_3 than water. Both solutions absorb CO_2 from the air.

When ammonia, NH_3, either in the gaseous state or in solution in water, combines with acids, a "direct" combination takes place. No hydrogen is displaced on either side, thus, $NH_3 + HCl = NH_4Cl$. The water solution of NH_3 acts very much like KHO or NaHO and is therefore termed a hydrate, supposed to be NH_4OH. The salts resemble K and Na salts very much, hence the "*um*" ending, which indicates that in combination NH_3 appears to act the part of a metal to some extent.

A red-hot platinum wire continues to glow in a mixture of air with ammonia gas, some oxides of nitrogen being formed and eventually nitrous and nitric acids. NH_3 does not burn in air but readily in oxygen with a yellow flame. Ammonia solution slowly oxidises on exposure to air, some nitrous acid being formed.

Some metals, as Na, K, Mg, decompose NH_3 when heated with the gas, giving off hydrogen and forming nitrides:

$$2NH_3 + 3Mg = Mg_3N_2 + 3H_2.$$

These nitrides are decomposed again by water into metallic oxide and NH_3. $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$. Some of this nitride is formed when Mg burns in air.

DRY REACTIONS.

Most ammonium salts, when heated in a dry-tube, volatilise, either entirely or partially. Salts with fixed acids, such as phosphoric acid, lose ammonia, NH_3. Salts of ammonium with volatile acids can be volatilised, either *with* decomposition, such as the nitrate, nitrite, sulphate, the latter with formation of nitrogen, water, ammonia, and sulphurous anhydride; with temporary dissociation only, such as the chloride, bromide, iodide: the latter salts, condensing again, for the most part unchanged, and are found in the upper part of the test-tube.*

* When solids vaporise on heating and condense again to solids on the cooler parts of the apparatus, the process is termed "**sublimation.**" It does not differ essentially from distillation.

REACTIONS IN SOLUTION.

All ammonium salts are soluble in water.

$PtCl_4$ produces a heavy yellow precipitate of ammonium platinic chloride, $2NH_4Cl,PtCl_4$. The precipitate is soluble in much water (hence there appears no precipitate from dilute solutions), but insoluble in alcohol and ether. Ammonium platinic chloride leaves on ignition *only* spongy platinum. (Distinction from potassium platinic chloride, which leaves spongy platinum and potassium chloride, $Pt + 2KCl$.)

Tartaric acid produces from a concentrated solution of ammonium chloride a white crystalline precipitate of hydrogen ammonium tartrate, resembling the potassium precipitate in its appearance. The two precipitates are readily distinguished on ignition. Hydrogen potassium tartrate leaves a carbonaceous residue, which is strongly alkaline, and the potassium carbonate which it contains dissolves in water. The other leaves merely a residue of carbon, devoid of any alkaline reaction.

Neutral or normal salts of some polybasic oxy-acids, *e.g.*, well dried alkaline borates, phosphates, readily decompose ammonium salts, especially when heated, with evolution of ammonia gas, and formation of acid salts. Calcium phosphate will also liberate NH_3, thus:—

$$Ca_3P_2O_8 + 2NH_4Cl = Ca_2H_2P_2O_8 + CaCl_2 + 2NH_3\text{; and}$$
$$Ca_2H_2P_2O_8 - H_2O = Ca_2P_2O_7.$$

This reaction distinguishes, therefore, between normal and acid salts of polybasic acids.

Ammonia gas is readily recognised, 1st, by its pungent odour; 2nd, by its turning red litmus paper blue; 3rd, by its combining with the vapour of volatile acids (such as hydrochloric acid) to form white fumes (NH_4Cl).

Nessler's test* for traces of ammonia.—If a potash solution of potassium mercuric iodide, $2KI,HgI_2$, be added to a fluid containing mere traces of ammonia or of an ammonium salt, a brown precipitate of dimercurammonium iodide, or a yellow to brown coloration is produced, according to the quantity of the ammonium compound present—

$$2(2KI,HgI_2) + 3KHO + NH_4HO = \underset{\text{Brown pp.}}{NHg''_2I,OH_2} + 7KI + 3OH_2.$$

Ammonium hydrate and carbonate, as well as various other ammonium compounds, *e.g.*, ammonium chloride, ammonium sulphide, are most useful reagents for analytical purposes.

Ammonium salts and nitrates and nitrites react with each other thus:—

$$NH_4Cl + KNO_3 = KCl + 2H_2O + N_2O,$$
$$\text{and } KNO_2 + NH_4Cl = KCl + 2H_2O + N_2.$$

In consequence it is possible that ammonia may escape detection

* For the preparation of Nessler's solution, see Appendix (Reagents).

in a mixture of this kind if the nitrate or nitrite be in excess and the mixture be heated.

4. **MAGNESIUM,** Mg''. Atomic weight, 24. Specific gravity, 1·75. Melting point, 750° C. Boils at about 1100° C. (?)—This metal is silver white, malleable and ductile, does not oxidise in dry air, but is readily acted upon by acids, and also decomposes water when boiled with it. It occurs in nature as oxide, in the mineral periclase, MgO; as hydrate in brucite, $Mg(HO)_2$; as carbonate in magnesite, $MgCO_3$; and in hydromagnesite, $3MgCO_3,Mg(OH)_2,3H_2O$; as double carbonate in dolomite, $CaCO_3,MgCO_3$, and mesitine spar, $MgCO_3,FeCO_3$; as sulphate in kieserite, $MgSO_4,H_2O$ (from Stassfurth salt), and in epsomite, $MgSO_4,7H_2O$; as silicate in peridote, Mg_2SiO_4, enstatite, $MgSiO_3$, steatite, $3MgSiO_3,SiO_2$, talc, $4MgSiO_3,SiO_2$, serpentine, $2MgSiO_3,Mg(OH)_2$, and in diopside, $CaSiO_3,MgSiO_3$; and as borate in boracite, $3MgB_2O_4,B_2O_3$.

EXPERIMENTS.

I. Mg. heated in tube generally inflames at about the melting point. A white oxide, MgO, is formed which is very light, but neither volatile or fusible. Placed in water it scarcely dissolves; placed on moist red litmus it just turns it blue. It dissolves in acids.

II. Boiled with water, hydrogen is slowly given off and $MgOH_2O$ formed, a white powder soluble in acids.

III. Heated with sulphur *to a high temperature* in a hard glass tube, a sulphide can be obtained, but in a test tube the glass gives way before this action begins.

IV. HCl acts very energetically, giving off hydrogen and forming $MgCl_2$. H_2SO_4, dilute, acts similarly, and the solution on evaporation gives crystals of $MgSO_4,7H_2O$, magnesium sulphate. Nitric acid acts more slowly; on evaporating this solution nearly all the nitrate is decomposed and MgO left.

V. Soda, NaOH, dissolves the metal forming white MgO and evolving H.

DRY REACTIONS.

Magnesium salts, as such, impart no colour to a non-luminous gas-flame. The most characteristic reaction for magnesia, in the dry way, is the pale rose colour which this oxide acquires on moistening it with cobaltous nitrate, and then igniting it once more strongly on charcoal.

This colour can, however, only be relied on when no other metallic oxides are present; and as magnesium salts do not colour the outer blowpipe flame, recourse must almost invariably be had to reactions *in* solution. Ignition of the sulphate on charcoal in the reducing flame yields the sulphide, MgS. Prolonged ignition of the carbonate yields the oxide, magnesia, MgO, which is almost insoluble in water. The chloride $MgCl_2$ also loses some chlorine on ignition in air. The nitrate is easily decomposed, oxide resulting.

REACTIONS IN SOLUTION.

Sulphate, chloride, nitrate, acetate dissolve in water.

Magnesia is not precipitated by ammonia in the presence of

ammonium chloride, because it forms a soluble double chloride.* In the absence of ammonium chloride, part of the magnesia is precipitated as hydrate, $Mg(HO)_2$, thus—

$$2MgCl_2 + 2NH_4HO = Mg(HO)_2 + \underset{\text{Soluble double chloride.}}{2NH_4Cl,MgCl_2}.$$

In the presence of a sufficient amount of ammonium chloride, the magnesium hydrate is at once decomposed into magnesium chloride; $Mg(HO)_2 + 2NH_4Cl = MgCl_2 + 2NH_4HO$, and no precipitation takes place, nor is the double chloride precipitated by ammonium, sodium, or potassium carbonates, unless the two latter be boiled for some time with the double salt. Hence magnesium cannot be precipitated in Groups III. and IV., provided a sufficient amount of ammonium chloride be present, and the solution be kept moderately dilute.

Potassium, sodium, calcium, and barium hydrates precipitate magnesium almost completely as white magnesium hydrate, nearly insoluble in cold and hot water. Ammonium chloride as well as other ammonium salts dissolve it readily, and if originally present in sufficient quantities, prevent its formation.

Ammonium oxalate gives after some time from moderately dilute solutions of magnesium salts, a white crystalline precipitate of a double oxalate of magnesium and ammonia; but not in the presence of excess of ammonium chloride. N.B.—In this case excess means very little more than necessary to form the "double" salt.

HNa_2PO_4 (hydrogen disodium phosphate) precipitates hydrogen magnesium phosphate, $HMgPO_4$.

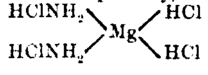
The precipitation is complete in the presence of ammonium chloride and ammonia NH_4MgPO_4, ammonium magnesium phosphate, being formed as a white crystalline precipitate. A very dilute solution should be gently heated and stirred with a glass rod. The precipitate deposits on the faint scratches caused by the glass rod on the tube. The precipitate is almost insoluble in water and ammonium salts. In water containing ammonia it is practically insoluble. Dilute mineral acids dissolve it, as well as acetic acid. From very dilute solutions the precipitate separates only on standing for about twenty-four hours in a warm place.

On heating magnesium chloride with precipitated mercuric oxide, the chloride is converted into oxide, mercuric chloride being volatilised. This experiment must be conducted in a closet which is provided with a good indraught of air, and is in connection with a chimney flue. Nearly a red heat is required.

Methods for the recognition and separation of Mg, K, Na, and Am will readily suggest themselves, if the student bear in mind—

* A number of compounds of this nature exist, but their "constitution" is not known with certainty, so they are provisionally termed "molecular" combinations or double salts.

This magnesium-ammonium salt is possibly,



1st. The volatility of ammonium salts (phosphates and borates excepted).
2nd. The insolubility of $Mg(HO)_2$ in water.
3rd. The insolubility of $2KCl,PtCl_4$ in alcohol.
4th. The intense yellow coloration sodium compounds impart to the blowpipe or Bunsen flame.

A solution containing salts of Mg, K, Na, and NH_3 may be examined as follows:

1st. Heat a portion with NaHO; ammonia gas is given off, which is recognised by its pungent odour and effect on red litmus paper = presence of NH_3.
2nd. To a second portion add ammonium chloride, ammonia, and sodium phosphate; a white crystalline precipitate indicates the presence of Mg.
3rd. *Evaporate a third portion to dryness and ignite strongly.* Extract with hot water (without filtering off any magnesium oxychloride (Mg_2OCl_2) which may have been formed), and add sufficient $Ba(HO)_2$ till the whole of the magnesium is precipitated as $Mg(HO)_2$; filter. To the filtrate add $(NH_4)_2CO_3$ as long as a precipitate is produced, and filter again. Evaporate the filtrate to dryness, and ignite strongly to expel ammonium salts. Dissolve the residue in a little water, filter off a trace of MgO (if any), and test filtrate for potassium by means of $PtCl_4$; a yellow crystalline precipitate = presence of K; *and for sodium, by heating on a platinum wire before the blowpipe flame; a golden-yellow flame indicates the presence of Na.*

It is, however, not necessary to get rid of magnesium before testing for potassium and sodium by the flame reactions or even by $PtCl_4$ for K.

The metals of this group are, chemically speaking, the most energetic elements of the metal class. They are able to turn out or displace most other metals from their compounds with oxygen, halogens, or acids. Magnesium is prepared by the action of sodium on the chloride $MgCl_2$.

Mg may also be used in many cases to obtain elements from their oxides or chlorides, *e.g.*, Sand; $SiO_2 + 2Mg = 2MgO + Si$. Many of these reactions can be performed in test tubes or in porcelain crucibles.

CHAPTER III.

REACTIONS OF THE METALS OF GROUP IV.

THIS group comprises the metals barium, strontium, and calcium, which are precipitated by ammonium carbonate from an ammoniacal solution in the presence of ammonium chloride. The latter (if present in sufficient quantity) prevents the precipitation of magnesium.

The three elements barium, strontium, and calcium are scarcely known in a metallic state. They resemble each other very closely in physical and chemical properties, and their compounds are often, indeed generally, found associated in nature.

	Atomic weight.	Sp. gr.	Melting point.
Ba . .	136·76	3·75	about that of cast iron.
Sr . .	87·39	2·54	at a red heat.
Ca . .	39·91	1·57	at a red heat.

The metals are not sensibly volatile at the highest furnace temperature. They appear to be volatile in the electric furnace. They all decompose water at the ordinary temperature, and oxidise rapidly, on the surface, in air. When heated to redness in air or oxygen they burn very brilliantly.

1. **BARIUM,** Ba″. Occurs in nature chiefly in the form of heavy spar, $BaSO_4$, and as witherite, $BaCO_3$.

DRY REACTIONS.

Barium compounds when held in the lower and outer part of a Bunsen gas burner or when heated on thin platinum wire in the inner blowpipe flame impart a yellowish-green colour to the outer flame, especially when previously moistened with strong hydrochloric acid. When viewed through the spectroscope (the chloride or chlorate show best, two green lines, Baα and Baβ, come out most intensely; Baγ is less marked. Besides these, there are numerous lines in the red and yellow, and one broad indistinct line in the blue, close to F of the solar spectrum.

Heavy spar heated on charcoal in the reducing flame is reduced to barium sulphide, BaS, which fuses readily. This reaction is made use of to prepare on a manufacturing scale soluble barium salts from the sulphate. Barium carbonate is decomposed only slowly even by ignition to a strong white heat.

EXPERIMENT.

Either of the reactions mentioned should be performed and salts made from the BaS or $BaCO_3$ for testing.

REACTIONS IN SOLUTION.

Barium salts are obtained by dissolving the native carbonate or witherite $BaCO_3$ in dilute acids.* Heavy spar is attacked by alkaline carbonates at a high temperature. By mixing, on a small scale, finely powdered barium sulphate with three to four times its weight of fusion mixture or sodium carbonate, and heating in a platinum crucible over a gas flame, it is converted into barium carbonate, thus:—

$$BaSO_4 + Na_2CO_3 = \underset{\text{Insoluble in water.}}{BaCO_3} + \underset{\text{Soluble in water.}}{Na_2SO_4}.$$

On extracting the fused mass with hot water and filtering, $BaCO_3$ is left, which is soluble in most acids.

The nitrate, chloride, chlorate and acetate are soluble in water. Solutions *should be dilute* when used for testing.

$(NH_4)_2CO_3$ (group-reagent) precipitates white barium carbonate, $BaCO_3$, soluble with decomposition in acids; somewhat soluble in ammonium chloride. With carbonic acid it forms a soluble acid carbonate ($BaCO_3, H_2CO_3$), which is reprecipitated on boiling with evolution of carbonic anhydride. Barium carbonate is partially decomposed by alkaline sulphates—*e.g.*, potassium sulphate, into barium sulphate and alkaline carbonate. The decomposition is complete in the presence of free carbonic anhydride. $SrCO_3$ and $CaCO_3$ are not changed, even on boiling with K_2SO_4.

Sodium or potassium carbonate, same precipitate.

KHO and NaHO, free from carbonates and sulphates (which they rarely are), give from highly concentrated solutions a voluminous precipitate of barium hydrate, $Ba(HO)_2$, soluble in water. A solution of the hydrate in water is known as baryta-water. It possesses a strong alkaline reaction and great affinity for carbonic anhydride for which it is used as a reagent.

NH_4HO gives no precipitate.

H_2SO_4, and all soluble sulphates, give on warming and especially in the presence of free acid, a white, heavy precipitate of barium sulphate, $BaSO_4$, even from very dilute solutions of barium salts. The precipitate is insoluble in water, dilute acids, and alkalies; soluble to a perceptible extent in boiling concentrated hydrochloric and nitric acids, and also in concentrated solutions of ammonium salts, but not if the precipitants are in excess; soluble also in concentrated boiling sulphuric acid, with formation of dihydrogen barium

* Dilute acids (HCl or HNO_3) should be employed, as the barium chloride and barium nitrate, which result from the action of these acids upon witherite, are insoluble in the concentrated acids. Normal acids are strong enough.

disulphate, $BaSO_4,H_2SO_4$. The presence of an alkaline citrate greatly interferes with its precipitation. Solutions of strontium or calcium sulphate (two sulphates which are but slightly soluble in water, especially the former) constitute the most characteristic tests for barium.

$BaSO_4$ requires about 400,000 parts of pure water for solution; $SrSO_4$, 7000 parts; whilst $CaSO_4$ dissolves in 390 parts of water at 35° C., and in 460 parts at 100° C., being in fact less soluble in hot than in cold water.

HNa_2PO_4 (hydrogen disodium phosphate) gives from neutral or alkaline solutions a white precipitate of hydrogen barium phosphate, $HBaPO_4$, readily soluble in dilute nitric, hydrochloric or acetic acid. Perceptibly soluble in ammonium chloride.

$C_2O_4(NH_4)_2$ (ammonium oxalate) gives from a moderately dilute solution of a barium salt, a white pulverulent precipitate of barium oxalate, C_2O_4Ba, soluble in dilute nitric or hydrochloric acid. Soluble also in oxalic and acetic acids when freshly precipitated.

K_2CrO_4 (potassium chromate) gives a bright lemon-yellow precipitate of barium chromate, $BaCrO_4$, even from very dilute neutral or moderately acid (acetic acid) solutions, readily soluble in nitric, hydrochloric or chromic acid (H_2CrO_4)—reprecipitated by ammonia. —(Distinction from strontium and calcium salts, which are not precipitated from dilute solutions if acetic acid be present.)

$2HF,SiF_4$ (hydrofluosilicic acid) gives a colourless crystalline precipitate of barium silicofluoride, BaF_2SiF_4, which subsides quickly, especially upon the addition of an equal bulk of alcohol. It is somewhat soluble in water and in dilute acids but insoluble in alcohol. (Distinction of barium from strontium and calcium salts, which give no precipitate even on the addition of alcohol.)

Soluble barium salts, constitute exceedingly useful reagents for the detection of several acids, on account of the metal barium forming many insoluble salts.

2. **STRONTIUM,** Sr''.—Occurs in nature as sulphate in the mineral celestine, $SrSO_4$; and as carbonate in strontianite, $SrCO_3$.

DRY REACTIONS.

Strontium compounds when heated on platinum wire in the inner flame, colour the outer flame intensely crimson. When the flame is viewed through the spectroscope, it shows a number of characteristic lines, more especially the Srβ and γ lines in the red and the line Srδ in the blue, which latter is particularly suited for the detection of strontium in the presence of Ba and Ca.

Celestine, $SrSO_4$, heated on charcoal in the reducing flame, is converted into strontium sulphide, SrS, from which the chloride may be prepared for blowpipe and other reactions, by treating the residue with hydrochloric acid. Strontium carbonate, heated in a platinum crucible, over a gas blowpipe, is almost completely converted into oxide after about 20 minutes' heating.

REACTIONS IN SOLUTION.

The nitrate, chloride, acetate, are somewhat more soluble than the corresponding Ba salts.

$(NH_4)_2CO_3$ (group-reagent) gives a white precipitate of strontium carbonate, $SrCO_3$, less soluble in ammonium chloride than the corresponding barium carbonate; soluble in dilute acids. Carbonic acid produces the soluble hydrogen strontium dicarbonate $SrCO_3,H_2CO_3$, which is decomposed on boiling into normal carbonate, carbonic anhydride, and water.

Sodium or potassium carbonate, same precipitate.

H_2SO_4, or a soluble sulphate, produces a white precipitate of strontium sulphate, $SrSO_4$. From dilute solutions a precipitate appears only after some time, especially if calcium sulphate be used as the precipitant. Heat assists the precipitation. The precipitate dissolves perceptibly in hydrochloric or nitric acid, but is insoluble in alcohol. It is insoluble also on boiling in a concentrated solution of ammonium sulphate $(NH_4)_2SO_4$, and a little ammonia. (Distinction between strontium and calcium.)

A solution of strontium sulphate in water is not precipitated by ammonium oxalate, but itself readily precipitates barium salts.

HNa_2PO_4 (hydrogen disodium phosphate) gives a white precipitate of hydrogen strontium phosphate, soluble in acids, including acetic acid.

$C_2O_4(NH_4)_2$ (ammonium oxalate) precipitates strontium salts more readily than barium salts. The white precipitate of strontium oxalate, C_2O_4Sr, is readily soluble in dilute nitric or hydrochloric acid; *somewhat soluble in ammonium salts and in oxalic or acetic* acid.

The chromate, $SrCrO_4$, is soluble in acetic acid and other acids, nearly insoluble in water and ammonia.

3. **CALCIUM,** Ca''.—Occurs in enormous quantity in nature, in combination with carbonic, sulphuric, silicic and phosphoric acids. In plants it occurs combined with carbonic, sulphuric, and phosphoric acids; in animals combined with phosphoric and carbonic acids. It is occasionally also found in minerals which result from the action of acids (such as nitric or arsenic acid) upon calc spar or chalk.

The principal calcium minerals are the various calcium carbonates, which differ in physical properties or in crystalline structure, such as calc spar, $CaCO_3$ (containing occasionally, barium, magnesium, iron, manganese, lead, *in variable proportions, and passing gradually into* baryto-calcite and dolomite, siderite, diallogite, and plumbo-calcite), arragonite, marble, limestone, chalk; the sulphates, such as gypsum, $CaSO_4,H_2O$, anhydrite, $CaSO_4$, alabaster, selenite; the phosphates, such as apatite, some containing both chlorine and fluorine; bone-earth, $Ca_3P_2O_8$, and fluor spar, CaF_2.

DRY REACTIONS.

Most calcium compounds, when heated in the inner flame of the

blowpipe, colour the outer flame yellowish-red; calcium phosphate and borate excepted. The presence of strontium entirely obscures the calcium reaction. The calcium spectrum shows, among other lines in the red and yellow, an intensely green line, Caβ, also an intensely orange line, Caα.

Calcium carbonate when strongly ignited becomes converted into caustic or quicklime, CaO, which reacts alkaline to test papers. It combines with water very eagerly, evolving much heat, and is converted into calcium hydrate, $Ca(HO)_2$ (slaked lime), which is less soluble in water than either barium or strontium hydrate. It is also more soluble in cold than in hot water. Calcium sulphate is converted into calcium sulphide, CaS, when ignited on charcoal in the reducing flame. It also reacts alkaline.

REACTIONS IN SOLUTION.

Calcium salts are readily prepared from pure calc spar or marble, by means of dilute acids. Many of its salts are soluble in water, the nitrate and chloride especially so, and are deliquescent.

$(NH_4)_2CO_3$ (group-reagent) precipitates white calcium carbonate, $CaCO_3$, which is bulky and amorphous at first, but on warming gently become rapidly crystalline. Calcium carbonate is somewhat soluble in ammonium chloride, especially when freshly precipitated. It is in fact partially reconverted on boiling into calcium chloride.

Sodium or potassium carbonate, same reaction.

H_2SO_4, or a soluble sulphate, precipitates from *concentrated* solutions of a calcium salt white calcium sulphate, $CaSO_4H_2O$ + Aq, soluble in much water, and still more soluble in acids. A precipitate is obtained on the addition of twice the volume of alcohol from solutions which are too dilute to be precipitated by sulphuric acid or by a soluble sulphate. Calcium sulphate dissolves readily on boiling in a concentrated solution of ammonium sulphate, especially if slightly alkaline with ammonia.

A solution of calcium sulphate precipitates both barium and strontium salts.

HNa_2PO_4 (hydrogen disodium phosphate) gives a bulky white precipitate of tricalcium phosphate, $Ca_3P_2O_8$, soluble in dilute hydrochloric or nitric acid, and soluble in acetic acid, especially when freshly precipitated; reprecipitated by ammonia.

Potassium chromate gives a precipitate only in strong and neutral or alkaline solutions.

$C_2O_4(NH_4)_2$ (ammonium oxalate) produces even from very dilute solutions of calcium salts a white pulverulent precipitate of calcium oxalate, C_2O_4Ca + Aq, readily soluble in hydrochloric or nitric acid; not perceptibly soluble in oxalic or acetic acid. On gentle ignition calcium oxalate breaks up into calcium carbonate and carbonic oxide gas, and on igniting very strongly, calcium oxide is left.

Soluble calcium salts, such as the chloride or nitrate, constitute

important reagents for the detection of organic acids, more especially dibasic acids, on account of the metal calcium forming insoluble salts with many of them.

SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM.

Barium minerals frequently contain strontium and calcium, and strontium minerals barium and calcium as well. One method of separating these metals may be based upon—

1st. The insolubility of $BaCl_2$ in absolute alcohol,* $SrCl_2$ and $CaCl_2$ being soluble.
2nd. The insolubility of $Ba(NO_3)_2$, and $Sr(NO_3)_2$ in absolute alcohol $Ca(NO_3)_2$ being soluble.

For this purpose a hydrochloric acid solution of the mineral containing Ba and Sr, or Sr and Ca, or possibly Ba, Sr, and Ca, is prepared, and the solution evaporated to dryness and gently ignited. (Strong ignition must be avoided, as $CaCl_2$ is slightly decomposed into an insoluble basic salt when heated in air) ($CaOCaCl_2$).

Barium is separated from strontium and calcium, by digesting the finely divided residue with absolute alcohol, and separating from the undissolved $BaCl_2$ by filtration.

Strontium is separated from calcium by evaporating or distilling off the absolute alcohol, which contains the $SrCl_2$ and $CaCl_2$; precipitating with ammonium carbonate, filtering, and converting the strontium and calcium carbonates into nitrates by means of dilute nitric acid. The solution of the two nitrates is evaporated to dryness on a water-bath and absolute alcohol added, when *calcium nitrate* is dissolved *out*, strontium nitrate being insoluble in absolute alcohol.

Several other methods for recognising and separating the metals of Group IV. will suggest themselves.

It is often necessary to ascertain whether one or two, or all the metals of this group are present in a solution. This can be done by adding to their neutral solution a solution of K_2CrO_4, or $2HF,SiF_4$. A yellow or a transparent crystalline precipitate indicates barium. To a portion of the filtrate add $CaSO_4$; a precipitate forms, perhaps only after some time, proving the presence of strontium; or the solution remains clear, in which case calcium only need be looked for, the presence of which is indicated by the precipitate which ammonium oxalate produces from another portion of the largely diluted solution. If both strontium and calcium are present, separation is necessary.

No difficulty will be experienced by the student in drawing up schemes of analysis based upon—

1st. The insolubility of $BaCl_2$ and $Sr(NO_3)_2$ in absolute alcohol.

* Methylated spirit that has been dried by standing over some fresh CaO and then distilled or even filtered will do.

2nd. The insolubility of $BaCl_2$ in absolute alcohol and that of $SrSO_4$ in a concentrated solution of $(NH_4)_2SO_4$.

3rd. The insolubility of BaF_2,SiF_4, or $BaCrO_4$, as well as of $SrSO_4$ in water; $CaSO_4$ being sufficiently soluble to be readily indicated by ammonium oxalate.

4th. A good plan is to make a solution of the three metals in acetic acid, and to add to this potassium chromate:

$BaCrO_4$ only is precipitated, the filtrate is now made acid with H_2SO_4 when $SrSO_4$ is precipitated; the filtrate from this on addition of oxalic acid, or ammonium oxalate, gives another precipitate of CaC_2O_4.

$BaCrO_4$ is yellow, the other two precipitates are white, but the solution may be yellow owing to excess of the potassium chromate.

The same mixture should be examined by all these processes, so as to get an idea of their relative accuracy. N solutions will be strong enough to bring out these differences.

The oxides of these metals do not fuse or vaporise even in the oxy-hydrogen blowpipe flame, but glow very brightly—become **luminous.**

They are not reduced by carbon in any ordinary furnace. In the "electric furnace" compounds of carbon are formed, termed Carbides. They are probably C_2M—as CaC_2. On contact with water these give an oxide and acetylene;

$$CaC_2 + H_2O = CaO + C_2H_2.$$

The melted chlorides of these metals on electrolysis, by carbon electrodes, give the metal and chlorine.

The operation can be performed in a small graphite crucible heated over a good Bunsen flame, using rods of gas carbon to lead in the current from 5 or 6 Bunsen or Grove cells.

Very small globules of the liberated metals attach themselves to the anode or negative carbon, and may, with difficulty, be obtained by rapidly removing the carbon and dipping into heavy petroleum.

CHAPTER IV.

REACTIONS OF THE METALS OF GROUP III. OR THE AMMONIUM SULPHIDE GROUP.

GROUP III. comprises the metals aluminium, chromium, iron, cobalt, nickel, manganese, zinc. The phosphates of these metals, and of magnesium, barium, strontium, and calcium are also precipitated if phosphoric acid be present.

To get an idea of the working of this group it is advised that some if not all the following exercises be performed:

1. Add to a centinormal solution containing cobalt nitrate, ferric chloride, and calcium phosphate, dissolved in a little dilute hydrochloric acid, a strong solution of ammonium chloride, and then ammonia. A precipitate is produced. Filter, and add to the filtrate ammonium sulphide. A further precipitation takes place; the precipitate is black.

This shows that some members of this group are precipitated by NH_4OH and NH_4Cl; others only on the addition of NH_4HS.

2. Add to a solution of ferric, chromic, and aluminic chlorides (Fe_2Cl_6, Cr_2Cl_6, and Al_2Cl_6) ammonium chloride and ammonia, till it is just distinctly ammoniacal, and boil for a few minutes. A bulky gelatinous precipitate is obtained. Filter. Add to the clear filtrate a few drops of ammonium sulphide: no further precipitation takes place.

Showing that iron, chromium, and aluminium are precipitated (as hydrates) from their saline solutions by NH_4Cl and NH_4OH alone, without the aid of NH_4HS. (Ammonium chloride has no share in the precipitation, but counteracts the solubility of the aluminium hydrate in excess of the precipitant and prevents the partial precipitation of magnesium and some metals of Group III. as hydrates if present in the solution.)

3. Dissolve some barium, strontium, calcium, and magnesium phosphates in dilute hydrochloric acid, and cautiously add to the solution ammonia. No precipitate is produced till the free acid has been neutralised (with formation of ammonium chloride), when the phosphates are reprecipitated. Filter and add ammonium sulphide to the filtrate. No further precipitation takes place.

This shows that the phosphates of the alkaline earthy metals are precipitated by ammonia alone.

4. Dissolve some phosphates of Ni, Co, Mn, Zn, and Fe^{iv} in

dilute hydrochloric acid.* To one portion of the solution add ammonium chloride and ammonia. A precipitate is formed. The phosphates are reprecipitated. Filter and add ammonium sulphide; a further precipitate is produced; showing that the phosphates of these metals are not entirely precipitated by ammonium chloride and ammonia.

These two reagents precipitate—

Aluminic hydrate and phosphate	Nickel phosphate
Chromic ,,	Cobalt ,,
Ferric ,,	Manganese ,,
	Zinc ,,
	Barium ,,
	Strontium ,,
	Calcium ,,
	Magnesium ,,

5. To a solution of the sulphates or chlorides (free from Fe) of Ni, Co, Mn, and Zn, add NH_4Cl in considerable excess, and then NH_4HO in slight excess. No precipitate is obtained because the NH_4Cl forms double chlorides of the metals which are not effected by NH_4HO.† To one portion of this solution add strong sulphuretted hydrogen water (or pass a current of sulphuretted hydrogen gas); a copious precipitate is produced, consisting of NiS and CoS (black), ZnS (white), and MnS (pale pink).

This shows that nickel, cobalt, manganese, and zinc salts are not precipitated by NH_4Cl and NH_4HO, but by NH_4HS.

On exposing the other portion of the solution for some time to the air, it is seen to turn turbid where it is in contact with the air. Shake the solution and the turbidity increases rapidly; showing that NH_4Cl and NH_4HO produce, under favourable conditions, a partial precipitation (owing to oxidation of the Mn compound).

6. To another portion of the solution of the phosphates of Ni, Co, Mn, Zn, and Fe (see 4), add the chloride, hydrate and sulphide of

* This solution may also be prepared by adding hydrogen disodium phosphate to solutions of the above metals as long as a precipitate forms, and dissolving the precipitate in a little hydrochloric acid.

† The chlorides of the metals Zn, Ni, Co, Mn also form compounds with dry ammonia, NH_3, as represented by the zinc compound, $ZnCl_2{}^{NH_3}_{NH_3}$. This is the most stable of any in the group. Its probable constitution is $Zn{}^{NH_2HCl}_{NH_2HCl}$. These metals and manganese also form compounds of the form $MnCl_2 2NH_4Cl$. Cr and Al also form similar compounds, but they are very unstable. The dry chlorides of Ba, Sr, Ca, and Mg. also unite with dry ammonia, as $CaCl_2 2NH_3$, as well as forming compounds with NH_4Cl. They are N_2H_4 *or hydrazine* compounds probably.

The Co and Mn compounds of this class oxidise very rapidly, Cr slower

On adding ammonium chloride and hydrate to chromium solutions a violet or purple-coloured solution is often obtained. This is undoubtedly due to the formation of a chrom-ammonium or hydrazine compound.

ammonium, without first separating by filtration the precipitate produced by NH_4Cl and NH_4HO. The phosphates of Co, Ni, Mn, Zn, and Fe, which may be considered as existing in the hydrochloric acid solutions as acid or hydrogen salts, are converted into sulphides, and ammonium phosphate is left in solution.

7. To a solution of Fe_2Cl_6 add NH_4Cl and NH_4HO. A reddish-brown precipitate of ferric hydrate, $Fe_2(HO)_6$, is produced, which on the addition of $(NH_4)_2S$, turns black.

This shows that iron is first precipitated as hydrate, and is subsequently converted into sulphide. Some sulphur is generally precipitated in this action. Chromium and aluminium are precipitated under the same circumstances as hydrates, as they do not form sulphides in contact with water.

It will thus be seen that the group-reagents NH_4Cl and NH_4HO, for reasons stated under 4 and 5, do not thoroughly separate some of the members of Group III. from the others. The three reagents* if added together precipitate:—

1. Sulphides—

FeS, CoS, NiS	black	MnS	pale pink or yellow
		ZnS	white.

2. Hydrates—

$Al_2(HO)_6$ white $Cr_2(HO)_6$ green.

3. Phosphates of Cr, Al, Ba, Sr, Ca, and Mg, white or nearly so.

* Add ammonia to a solution of barium, strontium, calcium (and magnesium) oxalates in dilute hydrochloric acid, as long as a white precipitate is obtained. The oxalates of the alkaline earths are reprecipitated more or less completely as soon as the hydrochloric acid which (as in the case of the corresponding phosphates) holds them in solution is completely neutralised.

The same applies to the fluorides, borates, tartrates, citrates, &c., of these earthy bases which are precipitated by NH_4HO, although in the presence of much NH_4Cl they are to a great extent held in solution.

Silicic acid and silicates, soluble in hydrochloric acid, are likewise acted upon by NH_4Cl and NH_4HO, gelatinous silica, and silicates, being precipitated.

Arsenates would also be thrown down here under the same circumstances, but in the ordinary course of procedure they are decomposed in the second group.

Notice particularly, that in order to avoid complicating the qualitative course, it is usually preferred to evaporate the hydrochloric acid filtrate from Group II. to complete dryness, with the addition, towards the end of the evaporation, of a little concentrated nitric acid, whenever ammonium chloride and hydrate produce a precipitate. By these means silicic anhydride, SiO_2, is left behind insoluble in acids; the fluorides and borates are for the most part decomposed; boric and hydrofluoric acid being set free or volatilised. Oxalates are destroyed with evolution of carbonic anhydride by the oxidising action of the nitric acid; and tartrates, &c., are broken up by gentle ignition into carbon and volatile gaseous products; ferrous salts are converted into ferric salts, and on extracting the ignited residue with a little concentrated hydrochloric acid, the metals are obtained in solution as chlorides, together only with the phosphates of the alkaline earths, earthy and metallic bases.—See Tables.

NICKEL, Ni'' and ^{iv}.—Occurs in nature as sulphide, NiS'', in capillary pyrites, hair nickel, or millerite; as arsenide, in arsenical nickel, As_2Ni, and in copper-nickel, As_2Ni_2; as antimonide, Sb_2Ni_2, in antimony nickel, combined with sulphide, as in nickel glance or grey nickel ore, As_2Ni,NiS_2, as antimony nickel glance, Sb_2Ni,NiS_2; also in the form of minerals, which are the result of the oxidation of other nickel minerals, *e.g.*, as nickel ochre, $Ni_3As_2O_8$, and emerald nickel, $NiCO_3,2NiO,6H_2O$, as silicate in Rewdanskite, and as nickel magnesium silicate in the important mineral garnierite.

The metal nickel is very much harder than iron, and exhibits a slight yellow tint on a fresh or polished surface. Its atomic weight = 57·93, specific gravity 8·9; it melts between 1450° and 1600° C. It does not oxidise appreciably at ordinary temperatures in air or in contact with water, but acts upon acids readily. It becomes decidedly magnetic, but in an inferior degree to iron.

EXPERIMENTS.

Metallic nickel can be obtained as wire or thin sheet. The electro-deposited metal is very suitable for these experiments.

I. Heated in the open tube a piece of bright nickel loses its lustre, but *no* detachable amount of oxide is formed in a moderate time, unless some pure oxygen be sent through the tube. The oxide formed adheres closely, but may be scraped off with a knife.

II. Water has no action below 100°.

III. Heated with sulphur, the action is somewhat slow. At a moderate temperature a grey-black sulphide is formed, NiS. It is crystalline, but not very fusible; insoluble in water; decomposed by acids.

IV. HCl dissolves the metal readily with evolution of hydrogen, which smells somewhat like coal-tar. The solution is bright-green; on evaporation a yellow solid, $NiCl_2$, is left. Sulphuric acts similarly, and gives green crystals of sulphate, $NiSO_4$.

Nitric acid gives a blue-green solution; red fumes evolved. Solution on evaporation leaves yellowish crystals of NiN_2O_6—very deliquescent. On heating to redness, a black oxide is left.

The oxide dissolves in acids but not in soda. Freshly precipitated $Ni(HO)_2$ dissolves, partly, in ammonia solution.

DRY REACTIONS.

When nickel compounds are heated on charcoal with dry sodium carbonate in the inner blowpipe flame, they are reduced to a grey metallic powder which is feebly magnetic. Heated on a borax bead, in the outer flame, they yield an intensely coloured glass, which appears hyacinth-red to violet-brown when hot, and reddish-brown when cold. On fusing a little nitre in the bead, the colour is changed to bluish or dark purple, whereby nickel compounds may be distinguished from iron. Heated in the reducing flame the colour of the borax bead disappears, and it assumes a turbid grey appearance, owing to finely divided particles of metallic nickel. The reactions with microcosmic salt are similar, but the bead becomes almost colourless when cold.

REACTIONS IN SOLUTION.

Chloride, nitrate, and sulphate are soluble. Nickel salts, containing water of crystallisation, are mostly green, and their solutions are green. When heated they lose water and change to yellow, and are amorphous when they have not been melted. *Comp.* COBALT, p. 36. A solution of both a nickel and a cobalt salt may be red, green, or colourless, according to the quantities present of each of the metals.

$(NH_4)_2S$ (group-reagent) gives a black precipitate of nickelous sulphide, NiS, soluble in excess of the reagent, especially in the presence of free ammonia or of yellow ammonium sulphide, forming a dark brown solution—good indication of nickel. The sulphide is slowly reprecipitated on boiling. The presence of ammonium chloride (or better still, ammonium acetate) assists the precipitation. Nickelous sulphide dissolves with difficulty in dilute hydrochloric acid, but readily in nitric acid or aqua regia.

SH_2 gives no precipitate in acid solutions, and a partial precipitate only from a salt of nickel with a mineral acid; but produces readily a precipitate from a solution of nickelous acetate, or a nickelous salt mixed with an alkaline acetate, especially on heating.

NaHO or KHO precipitates from cold solutions an apple-green coloured hydrate, $Ni(HO)_2$, insoluble in excess, soluble in ammonium salts to a greenish-blue fluid. Nickelous hydrate leaves on ignition nickelous oxide. It does not absorb oxygen from the air.

NH_4OH produces a slight greenish precipitate, readily soluble to a blue fluid. No precipitate in presence of ammonium chloride owing to a double being formed.

Na_2CO_3 precipitates an apple-green basic carbonate, varying in composition.

NH_4HCO_3 same precipitate, readily soluble in excess, after washing, to a greenish-blue solution.

KCy* gives a yellowish-green precipitate of nickelous cyanide, $NiCy_2$, which dissolves readily in excess of potassium cyanide to a brownish-yellow solution, containing a double cyanide of nickel and potassium, $2KCy,NiCy_2$. On adding a dilute acid (HCl or H_2SO_4), $NiCy_2$ is reprecipitated, and the KCy is decomposed with evolution of HCy. Boiling with hydrochloric acid decomposes the nickelous cyanide also.

The solution of the double cyanide is not altered by boiling with excess of HCy, but the nickelous salt is oxidised in the cold by a concentrated solution of sodium hypochlorite, ClNaO, or chlorine or bromine water, to black nickelic hydrate, $Ni_2(HO)_6$, which is gradually precipitated; thus:

$$2NiCy_2 + ClNaO + 5OH_2 = Ni_2(HO)_6 + NaCl + 4HCy.$$

Nickelic hydrate may also be obtained by passing chlorine through

* Potassium cyanide is seldom pure enough to give this reaction cleanly The salt should be recrystallised from alcohol when required for this test.

water in which nickelous hydrate is suspended. HCl decomposes the higher oxidised compound into nickelous chloride and free chlorine. Nickelic oxide, Ni_2O_3, obtained by igniting the hydrate, or by keeping the nitrate at a temperature of about 200° C., is a black substance, scarcely soluble in boiling acetic acid.

COBALT, Co'' and iv.—Occurs in nature as sulphide, or cobalt pyrites, Co_2S_3; as arsenide in As_2Co, tin-white cobalt or smaltine (speiss cobalt); as sulpharsenide or cobalt glance, As_2Co,CoS_4: also in the form of products of oxidation, such as cobalt vitriol, $CoSO_4,7H_2O$; as arsenate, $Co_3As_2O_8 8OH_2$, in cobalt bloom. Cobalt is generally found in small quantity in most nickel and iron ores. It resembles the metal nickel very closely, so much so that it may almost be looked upon as an isomeric form of that element. Its atomic weight = 58·89. Specific gravity 8·6. Melting point about 1800 C. It is slightly redder in tint than Ni, and when pure behaves similarly to Ni as regards air and water. It is also a little harder. Acids act upon it about as readily as in the case of nickel. It also becomes slightly magnetic. Cobalt is not so abundant nor is it so much used as nickel.

EXPERIMENTS.

These results are to be compared with those from nickel.

Metallic cobalt can be obtained in thin electro-deposited plates, or in small pieces from fusion.

I. Heated in air, the metal becomes covered with a film of oxide, but slowly.

II. Water has no action at 100°.

III. Sulphur combines slowly, forming black CoS.

IV. Acids act with about the same ease as on nickel. With HCl the solution is pink, and becomes blue on evaporating; finally a blue mass of $CoCl_2$ is left. It is very soluble in water.

H_2SO_4 acts similarly, when not too dilute, and heated. On evaporating nearly to dryness, red crystals of $CoSO_4$ are formed.

HNO_3 acts more rapidly. The solution is pink when dilute, and blue when concentrated, and on complete evaporation a blue, very deliquescent mass is left. Further heating gives black oxide, Co_3O_4. This is soluble in acids, and gives the same salts as from the metal. The nitrate is $CoN_2O_6 + Aq$.

V. Alkalies have no action either on metal or oxide. Ammonia only affects the hydrate $Co(HO)_2$.

DRY REACTIONS.

Cobalt is usually detected with comparative facility. Cobalt minerals containing sulphur or arsenic are roasted on charcoal, or in a glass tube, when sulphurous and arsenious anhydrides are evolved. The residue is then introduced into a borax bead, and heated in the outer flame, when a fine blue coloured bead is obtained. This colour remains the same both in the outer and inner, or reducing flame. In cases where much Mn, Fe, Cu, or Ni are mixed with Co, the blue appears distinctly only after the bead has been heated for some time in the reducing flame. Microcosmic salt gives a similar blue bead. Heated on charcoal, with sodium carbonate, in the reducing flame,

cobalt separates as a grey metallic powder, which is attracted by the magnet. Potassium cyanide is better than carbonate for this.

REACTIONS IN SOLUTION.

Cobalt salts are mostly red or pink when crystalline and hydrated. The solutions are also red. When dehydrated by heating, they become blue. The solutions also when concentrated and warm are blue, and go pink on cooling or diluting. *Comp.* NICKEL, p. 34.

$(NH_4)_2S$ (group-reagent) gives a black precipitate of cobaltous sulphide, CoS, insoluble in excess of the reagent, and very difficultly soluble in dilute hydrochloric or sulphuric acid, but readily soluble in aqua regia upon the application of heat. Hence a black residue left, on treating the ammonium sulphide precipitate of Group III. with dilute hydrochloric acid, indicates probably the presence of cobaltous or nickelous sulphide.

SH_2 gives no precipitate from an acid solution, but precipitates cobaltous sulphide partially from a neutral solution, and wholly from a solution of cobaltous acetate, or from a solution of a cobaltous salt containing a mineral acid on the addition of an alkaline acetate.

KHO or NaHO gives a precipitate of a blue basic salt, which turns olive-green on exposure to air, owing to the absorption of oxygen. On heating in very dilute solutions, a rose-red cobaltous hydrate, $Co(HO)_2$, is obtained, which, however, often contains a small amount of dark brown cobaltic hydrate. Ammonium carbonate dissolves the precipitate (after filtration and washing) to an intensely violet-red fluid. This is a cobaltamine.

By suspending cobaltous hydrate in water, and passing a current of chlorine into it, black cobaltic hydrate is precipitated, cobaltous chloride remaining in solution, thus:

$$3Co(HO)_2 + Cl_2 = \underset{\text{Cobaltic hydrate}}{Co_2(HO)_6} + CoCl_2.$$

In the presence of an alkali (NaHO) the whole of the cobaltous hydrate is converted into cobaltic hydrate. Br or I act as well as Cl.

NH_4HO produces in neutral solutions a slight precipitate of a basic salt, which dissolves readily in excess. The solution is reddish-brown. Ammonium chloride prevents the precipitation altogether. The solution, however, absorbs oxygen from the air, and becomes red on standing.

Na_2CO_3 precipitates a peach-coloured basic carbonate.

$(NH_4H)_2CO_3$ same precipitate; readily soluble in excess to a red solution.

KCy gives with all neutral cobaltous salts a brownish-white precipitate of cobaltous cyanide, $CoCy_2$, soluble in excess, reprecipitated by dilute hydrochloric or sulphuric acid.

N.B.—In case the cobaltous solution should contain free acid, so that it liberate hydrocyanic acid by the action of the latter upon the excess of KCy, also if the solution containing the double cyanide

$2KCy,CoCy_2$, be heated in the air for some time, dilute hydrochloric or sulphuric acid will no longer produce a precipitate, the whole of the cobaltous cyanide having been converted into cobaltic cyanide Co_2Cy_6, which remains combined with 6KCy to form a well-defined and stable salt, called potassium cobalticyanide, $K_6Co_2Cy_{12}$, hydrogen being evolved, thus:

$$2CoCy_2 + 2HCy = Co_2Cy_6 + H_2.$$
$$6KCy + Co_2Cy_6 = \underset{\text{Potassium cobalticyanide.}}{K_6Co_2Cy_{12}}$$

This salt is not acted upon by a cold solution of sodium hypochlorite. It corresponds closely to potassium ferricyanide. *Comp.* IRON.

Separation of Nickel from Cobalt.—The hydrocyanic acid reaction affords a good method of separating nickel from cobalt. To a slightly acid solution of the two salts add cautiously, drop by drop, a solution of potassium cyanide as long as a precipitate forms, and till the precipitate is just redissolved and the yellowish-brown turbid liquid has become clear. Boil for some time in a well-ventilated place, to avoid inhaling fumes of HCN which escape, allow to cool, and add a moderate quantity of bromine water, chlorine water, or a hypochlorite as bleaching powder solution will do as well, and then NaOH; $Ni_2(HO)_6$ is precipitated on gently warming, and cobalt remains in solution as $K_6Co_2Cy_{12}$. Separate by filtration. Test the residue in a borax bead for nickel, and evaporate a part of the solution to dryness and test for cobalt by means of a borax bead.

Instead of separating nickel as $Ni_2(HO)_6$ by means of hypochlorite or Br water and NaOH, the solution, after digesting with excess of HCy or KCy, may also be precipitated whilst hot with freshly precipitated and washed mercuric oxide. On digesting for a short time at a gentle heat, the whole of the nickel is precipitated, partly as $Ni(HO)_2$, partly as $NiCy_2$ the mercury combining with the liberated cyanogen. Filter off the greenish or yellowish-grey precipitate, wash and ignite. Pure NiO is left; thus:

$$(1)\ NiCy_2 + HgO + OH_2 = HgCy_2 + \underset{\text{Greenish precipitate.}}{Ni(HO)_2,NiCy_2}$$

$$(2)\ Ni(HO)_2,NiCy_2 + HgO + = 2NiO + \underset{\text{Volatile on ignition.}}{HgCy_2} + OH_2$$

The cobalt remains in the solution as $K_6Co_2Cy_{12}$. Nearly neutralise with dilute nitric acid, and add a neutral solution of mercurous nitrate, $Hg_2(NO_3)_2$. A white precipitate of mercurous cobalticyanide, $Hg_6Co_2Cy_{12}$, forms, which contains the whole of the cobalt. Filter, wash, and ignite under a hood with free access of air, when tricobaltic tetroxide, Co_3O_4, is left.

Another method of separation consists in adding a concentrated

solution of pure KNO_2 (potassium nitrite) in considerable excess to a concentrated neutral solution of the two metals, then acetic acid until acid to test paper. On keeping the solution in a moderately warm place, the nickel salt remains in solution, and the whole of the cobalt separates in the form of a crystalline precipitate of a fine yellow colour (from a dilute solution only after long standing), the formation of which is expressed by the equation:

$$2CoN_2O_6 + 14KNO_2 + 4\left\{\begin{matrix}CH_3\\COOH\end{matrix}\right. + OH_2 =$$

$$\underset{\text{Yellow precipitate}}{Co_2 6(NO_2), 6KNO_2, 3OH_2} + 4KNO_3 + 4\left\{\begin{matrix}CH_3\\OCOK\end{matrix}\right. + N_2O_2.$$

The precipitate is perceptibly soluble in cold, and more readily still in hot water; it is decomposed by hot nitric or hydrochloric acid, or by potassium hydrate; insoluble in alcohol and in the presence of potassium acetate; and it can therefore be washed by a *solution of potassium acetate, and finally with alcohol.* This reaction separates nickel from cobalt very effectually.*

From the filtrate the nickel is best precipitated as the apple-green basic carbonate by a fixed alkaline carbonate.

The presence of Ba, Sr, or Ca salts interferes with the reaction, as it gives rise to the precipitation of triple nitrites of Co, Ni, and one of the other metals. Nickel forming similar compounds with Ba, Sr, or Ca, that cobalt forms with alkaline metals.

On igniting $Ni(CO_3)_2$, a dirty greyish powder of NiO is left. $Co(NO_3)_2$, heated gently at about 200° in an air-bath, leaves black cobaltous dicobaltic tetroxide, Co_3O_4, which is not soluble in boiling dilute acetic acid. On treating this oxide with hydrochloric acid, chlorine gas is evolved, according to the equation:

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + 4OH_2.$$

Both nickel and cobalt are capable of forming compounds in which the metals exist in a tetrad condition, viz.:

Ni_2O_3,	Co_2O_3,	and	Co_2S_3.
Nickelic oxide	Cobaltic oxide		Cobaltic sulphide.

Ni_2O_3 is, however, mostly obtained in the presence of water by the action of oxidising agents, and cannot exist at a high temperature.

Co_3O_4, on the other hand, is obtained in the dry way, or on gentle ignition of cobaltous salts containing volatile acids, and gives up a portion of its oxygen only on strong ignition.

The same tendency to form a compound in which cobalt exists as a tetrad element is observed on exposing the freshly precipitated hydrate to the air, or on passing chlorine or adding bromine or iodine to cobaltous solutions.

Little use has been made of these reactions for analysis purposes

* This reaction can evidently not be used for hurried work.

beyond the conversion of $CoCy_2$ into Co_6Cy_6, in the presence of potassium cyanide, or of CoO into Co_2O_3 in the potassium nitrite reaction.

MANGANESE, Mn'', iv, and vi.—Occurs in nature in various states of oxidation, forming oxides, of which the mineral pyrolusite, MnO_2, is the most important. It is found in small quantities in many iron ores, and is a frequent constituent of silicates: the MnO replacing the isomorphous bases, FeO, ZnO, MgO, CaO, without altering the crystalline structure of the minerals. It exists both in the dyad and tetrad condition in manganous and manganic oxides. The anhydrous oxides known, besides pyrolusite, are braunite, Mn_2O_3, hausmannite, Mn_3O_4; the hydrates are: manganite, Mn_2O_3,H_2O, psilomelane, wad, varvicite, copper-mangan, &c. Manganese is found in combination with sulphur in manganese blende, MnS; with carbonic acid in diallogite, $MnCO_3$; with silica in red manganese or mangan kiesel (rhodonite), $MnSiO_3$; and in tephroite, Mn_2SiO_4; with phosphoric acid as triplite, $Mn_2Fe_2P_2O_9$.

Manganese is not used exactly in the pure metallic state, but is largely employed as an alloy with iron, as spiegeleisen, manganese steel, and in some bronzes, &c. It can, however, be obtained as a crystalline or granular powder, in which state it is sometimes used for preparing alloys, with copper and other metals. It generally contains some combined carbon. It generally imparts considerable hardness to alloys. It is not magnetic. Atomic weight 54·8; specific gravity 8·0. It melts at about 1900° C. It oxidises very rapidly in air and water, and dissolves in most acids.

EXPERIMENTS.

With the ordinary oxide, MnO_2.

I. Heated in a tube, shows very little change, but at a high temperature it is possible to get some oxygen evolved which will relight a glowing splinter of wood.

II. Water has no action.

III. Heated strongly with sulphur some SO_2 is given off and a sulphide formed which fuses at a high temperature (difficult to get).

IV. HCl dissolves MnO_2 (and other oxides); chlorine is evolved on heating. On evaporating, a pale pink mass of $MnCl_2$ is left.

H_2SO_4 requires heating strongly; the action is slow, and oxygen is given off.

HNO_3 is practically without action.

Alkalies are without action in solution, but when melted form a green mass of alkaline manganate.

I. With the metal. Metallic Mn powder heated in the tube oxidises, frequently glowing and forming a red or brown powder.

II. HCl dissolves the metal slowly, giving off H, which contains some hydro-carbon. Diluted nitric and sulphuric also dissolve it, but the concentrated acids have little action.

III. The finely powdered metal oxidises very rapidly when dropped into melted nitre.

DRY REACTIONS.

The presence of manganese is readily detected in minerals which contain no other oxides capable of colouring fluxes, as they dissolve when heated in the outer flame, in the borax bead, or in a bead of

microcosmic salt, to a clear violet-red colour, which becomes of a fine amethyst colour on cooling. The bead becomes colourless when heated in the reducing flame. If other metallic oxides are present, it is preferable to mix a small trace of the finely powdered manganese compound with two or three times its weight of sodium carbonate (a little nitre should also be added), and to fuse on platinum foil (a small platinum spoon or the lid of a platinum crucible) in the oxidising flame, or over the tip of the Bunsen, when a bluish-green mass is left after cooling, consisting of sodic manganate, Na_2MnO_4. The mass at the same time loses its transparency. This forms the most characteristic and delicate reaction for manganese. Manganous and manganic oxides are converted by this treatment into a higher oxide, MnO_3, or perhaps Mn_2O_7.

REACTIONS IN SOLUTION.

The sulphate and chloride are soluble. The nitrate is scarcely known. Solid hydrated manganous salts are pinkish in colour.

All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into manganous chloride. The chlorine so evolved is a measure of the amount of MnO_2 present in a manganese ore.

Dilute solutions of pure manganous salts (free from manganates or permanganates) are colourless.

$(NH_4)_2S$ (group-reagent) gives a flesh-coloured precipitate of manganous sulphide, MnS, readily soluble in dilute acids, even acetic acid. Hence the presence of free acetic acid prevents the precipitation of manganese by SH_2 (method of distinguishing Co and Ni from Mn). The manganese may be separated by repeating once or twice the precipitation of cobalt and nickel in the presence of acetic acid.

SH_2 does not precipitate a neutral solution of a manganous salt; the acetate is acted upon but very slowly and imperfectly, and not at all when free acetic acid is present.

KHO or NaHO gives a white precipitate of manganous hydrate, $Mn(HO)_2$, insoluble in excess. The precipitate speedily absorbs oxygen from the air, and turns dark brown with formation of Mn_2O_3,H_2O, which then no longer dissolves completely in ammonium chloride.

NH_4HO precipitates a white hydrate from neutral solutions; insoluble in excess, or in ammonium carbonate. It rapidly absorbs oxygen.

No precipitate is produced in solutions containing ammonium chloride. On exposing an ammoniacal solution of the soluble double chloride, $2NH_4Cl$, $MnCl_2$, to the action of the air, the whole of the manganese is gradually precipitated as dark-brown manganic hydrate, Mn_2O_3,H_2O. This reaction is characteristic for manganese compounds and distinguishes it from zinc, nickel, &c.

In this change the ammonium hydrate conveys oxygen to the manganous salt in a manner similar to the action it has upon cobaltous salts, or upon metallic copper, in the presence of oxygen or air.

Owing to this tendency of manganous salts to become oxidised and precipitated *in the presence of free ammonia*, it is not possible to completely separate manganous from ferric salts by means of ammonium chloride and hydrate. The reddish-brown ferric hydrate, which is precipitated, invariably carries down more or less Mn_2O_3,H_2O; and small quantities of manganese cannot, therefore, be separated from iron by precipitation with these reagents. The separation succeeds best if the excess of ammonia be immediately boiled off.

Na_2CO_3 or K_2CO_3 precipitates white manganese carbonate, $MnCO_3$, insoluble in excess of the reagent, but pretty readily soluble in ammonium chloride. This precipitate also absorbs oxygen from the air, and turns to a dirty brownish-white colour, owing to the formation of manganic hydrate. On ignition with free access of air, the white carbonate turns first black, and changes subsequently to brown trimanganic tetroxide, Mn_3O_4. All manganese oxides are finally obtained upon ignition in the air in the form of Mn_3O_4. Both Mn_2O_3 and Mn_3O_4 are compounds of MnO with MnO_2.

KCy gives a whitish precipitate of manganous cyanide, $MnCy_2$, soluble in excess to a brown solution, which is not precipitated by ammonium sulphide.

Manganous compounds, soluble or not, are very readily oxidised in contact with water and chlorine, bromine, or iodine, or a hypochlorite to MnO_2H_2O:

$$MnCl_2 + ClNaO + 2OH_2 = MnO_2,H_2O + NaCl + 2HCl.$$

By fusion with dry sodium carbonate, alone or together with nitre, the manganous or manganic compounds are converted into an alkaline manganate, in which the metal manganese acts the part of a hexad element. Only the alkaline manganates dissolve in water giving green solutions.

Manganates are readily decomposed in aqueous solutions. On gently heating a solution of potassium manganate with free access of air, the green colour changes to purple-red, owing to the formation of potassium permanganate, $K_2Mn_2O_8$, and separation of hydrated dioxide and alkaline hydrate, thus:

$$3K_2MnO_4 + 3OH_2 = K_2Mn_2O_8 + MnO_2,H_2O + 4KHO.$$

The change is accelerated by adding a few drops of a dilute mineral acid, *e.g.*, nitric, hydrochloric, or sulphuric acid, which combines with the liberated alkali and manganese oxide.

The manganese seems to act here the part of a pseudo-octad element; and it may readily be inferred that the different oxygen atoms perform different functions in such a highly oxygenised compound, and that the manganese will part with some more readily than with others.

Manganic dioxide, as well as other peroxides, also the alkaline manganates and permanganates, act as powerful oxidisers, differing merely in the extent of their oxidising action.

Manganic dioxide gives off oxygen on warming with concentrated sulphuric acid, and forms normal manganous sulphate :

$$2MnO_2 + 2H_2SO_4 = O_2 + 2MnSO_4 + 2OH_2.$$

Sulphuric acid added to sodium, or other manganate, gives off oxygen, and forms sulphates thus :

$$Na_2MnO_4 + 2H_2SO_4 = O_2 + MnSO_4 + Na_2SO_4 + 2OH_2.$$

Sulphuric acid added to a solution of potassium permanganate, liberates five atoms of oxygen, and leaves manganous and potassium sulphates in the solution when something is present capable of taking up the oxygen.

$$2K_2Mn_2O_8 + 6H_2SO_4 = 5O_2 + 4MnSO_4 + 2K_2SO_4 + 6OH_2.*$$

Hydrochloric acid also acts upon the higher oxides of manganese, with evolution of chlorine and formation of metallic chlorides and water. Potassium permanganate and hydrochloric acid form the most convenient chlorine "generator" on a small scale. The peroxides of manganese, especially the black oxide, constitute the principal substances, used together with hydrochloric acid, or sodium chloride and oil of vitriol, for evolving chlorine in the laboratory and on a manufacturing scale.

No other mineral oxidising agent is capable of yielding from one molecular group of elements five atoms of oxygen; and there are but few substances which resist the oxidising action of potassium permanganate. Hydrogen, freshly ignited charcoal, phosphorus, iodine, sulphur, sulphuretted hydrogen, carbon disulphide, hydrocarbons and organic bodies generally, are oxidised more or less rapidly. Metals, such as zinc and iron (when alkaline the action is slow if at all on iron) become oxidised after a few days; lead, copper, mercury and silver, a little slower. Many lower oxides, chlorides, &c., are converted into higher oxides, &c., especially in the presence of a free acid (hydrochloric or sulphuric).

Thus arsenious is converted into arsenic acid, sulphurous into sulphuric, nitrous into nitric, phosphorous into phosphoric acid. Oxalic acid is oxidised into carbonic anhydride and water. Lower or -ous chlorides, sulphates, &c., are converted into the higher or -ic salts, *e.g.*, ferrous, stannous, antimonious, cuprous, and mercurous

* Note. This equation is true if the permanganate be added to hot moderately strong sulphuric acid. When added, in powder, to cold concentrated H_2SO_4, the first reaction is

$$K_2Mn_2O_8 + H_2SO_4 = K_2SO_4 + H_2O + Mn_2O_7.$$

This substance Mn_2O_7 collects in oily drops on the sulphuric acid. They have a beetle-green lustre, and give off a pink vapour. Contact with almost any kind of combustible substance, as S. P. alcohol, &c., will cause a violent explosion. *Very little* of this substance must be made at once, as a slight elevation of temperature also causes violent decomposition. The substance distils over along with steam.

chlorides are oxidised or "chlorinised" in the presence of free hydrochloric acid into ferric, stannic, antimonic, cupric, and mercuric chlorides; the manganese and potassium of the permanganate are left in solution as chlorides. Ferrous, cuprous, and other sulphates are converted in the presence of free sulphuric or hydrochloric acid into ferric, cupric, &c., sulphates.

The reaction in all these cases is indicated by a change of colour. On adding, for instance, the purple-coloured permanganate solution to a solution of sulphurous acid, the colour is instantly destroyed as long as any sulphurous acid is left. Permanganate is a quantitative measure for sulphurous acid, and in like manner for other lower oxides, chlorides, organic bodies, &c.

Sulphurous acid requires one atom of oxygen in order to be converted into sulphuric acid; as one molecule of potassium permanganate can part with five atoms of oxygen, one molecule of the oxidising agent oxidises five molecules of the reducing agent, *i.e.*, 316 parts by weight of potassium permanganate are the measure for $5 \times 64 = 320$ parts by weight of SO_2.

Two molecules of ferrous sulphate in the presence of sulphuric acid combine with one atom of oxygen to form one molecule of ferric sulphate, thus:

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

Hence one molecule of potassium permanganate oxidises ten molecules of $FeSO_4$, ten molecules of FeO, or ten atoms of Fe; so that 316 parts by weight of $K_2Mn_2O_8$ are a measure for—

10×152	parts by weight of	$FeSO_4$
or 10×72	,,	FeO
or 10×56	,,	Fe.

ZINC, Zn″.—Occurs in nature chiefly as sulphide or zinc blende, black jack, ZnS; as carbonate, or calamine, $ZnCO_3$; and as silicate, or zinc glance, electric calamine, Zn_2SiO_4,OH_2, willemite, Zn_2SiO_4; also as oxide in red zinc ore, ZnO. The red colour is due to Fe and Mn.

The metal being volatile at a high temperature is extracted from its oxide by distillation with carbon. It is of a decided blue tint; highly crystalline, and somewhat brittle when cold, but becomes malleable when heated to about 120° C. Its atomic weight = 64·90; specific gravity 7·15; melting point 360° C.; boiling point, about 1040° C. It oxidises superficially in air, and decomposes water slowly at its boiling point (100° C.), and steam rapidly at a red heat. It dissolves in most acids, displacing two equivalents of hydrogen.

EXPERIMENTS.

I. Metallic zinc heated in the open tube melts; a film of oxide forms over the surface, which appears wrinkled. On further heating the metal begins to vaporise and burns with a bluish flame; a deposit of oxide is formed on the

tube. This oxide, ZnO, is yellow whilst hot and white on cooling. It does not melt or vaporise.

II. Water has little visible action below 100°.

III. Just melted with sulphur very little action takes place, or only a superficial one. Strongly heated, to vaporising in a hard tube, a somewhat energetic combination takes place. It is best to heat up quickly over a blowpipe.

IV. HCl and H_2SO_4 (dilute) dissolve the metal rapidly, evolving hydrogen. The sulphuric acid solution on evaporation easily gives white crystals of $ZnSO_4, 7H_2O$. The HCl solution on evaporation yields a syrupy body, $ZnCl_2$, which at a red heat gives off whitish vapours. On cooling it sets into a white or sometimes glassy mass. It is *extremely* deliquescent and soluble.

Nitric acid acts very rapidly; red fumes are evolved The solution contains ZnN_2O_6, which is left on careful evaporation as a similar substance to the chloride.

Alkalies dissolve the metal on heating, liberating hydrogen and forming white compounds as $ZnOK_2O$. If Fe or Pt be present the action is more vigorous.

The oxide dissolves very easily both in acids and alkalies, including ammonia hydrate.

DRY REACTIONS.

The most characteristic blowpipe reaction for zinc consists in the white incrustation of zinc oxide which its compounds yield when heated on charcoal in the reducing flame with sodium carbonate. The zinc compound is reduced to the metallic state, and the metal being volatile, burns, on passing through the outer flame, with a bluish-green flame and is converted into oxide, which covers the charcoal with an incrustation, yellow when hot, white when cold, and which assumes a fine green colour when treated with a solution of cobaltous nitrate, and once more strongly heated in the outer flame. The incrustation is not driven away in the oxidising flame —zinc oxide being non-volatile.

Zinc compounds give with borax or microcosmic salt in both flames a bead, which is yellowish whilst hot, and white on cooling; opaque if much zinc salt be present. This applies, however, only to pure zinc compounds, and the detection of zinc by the blowpipe in poor ores containing other readily oxidisable metals (such as Pb, Cd, As, Sb, which give likewise incrustations) is a matter of great uncertainty. The borax bead is quite unreliable for zinc.

Zinc sulphide (zinc blende), when roasted in a tube of hard glass, loses part of its sulphur in the form of sulphurous anhydride, and forms some zinc sulphate, $ZnSO_4$ (white vitriol), which may be extracted with water.

Both calamine and blende on thorough roasting leave zinc oxide.

REACTIONS IN SOLUTION.

Most zinc salts are soluble in water, the chloride and nitrate extremely so. They are only coloured when the acid is coloured or a chromogen.

$(NH_4)_2S$ (group-reagent) gives a white precipitate of zinc sulphide, ZnS, insoluble in excess. From dilute solutions the precipitate separates only after some time, but more speedily in the presence of

ammonium chloride. It is readily decomposed by dilute hydrochloric and sulphuric acids, with the evolution of sulphuretted hydrogen; also by nitric acid, but is insoluble in acetic acid.

SH_2 precipitates zinc imperfectly from neutral solutions of zinc salts with mineral acids; but from an acetate or a solution of a zinc salt mixed with an alkaline acetate, the whole of the metal is precipitated by sulphuretted hydrogen as zinc sulphide, even in the presence of much acetic acid. (Method of separation of Zn from Mn.)

KHO or NaHO precipitates the white hydrate, $Zn(HO)_2$, readily soluble in excess, also in ammonia; reprecipitated almost entirely on largely diluting with water and boiling; soluble also in ammonium chloride. Sulphuretted hydrogen precipitates the whole of the zinc from these solutions. In the presence of the hydrates of manganese, nickel and cobalt, KHO or NaHO does not readily dissolve out the whole of the zinc hydrate.

Na_2CO_3 or K_2CO_3 produces a white precipitate of basic carbonate, consisting of two molecules of zinc carbonate and three molecules of zinc hydrate, according to the equation:

$$5ZnSO_4 + 5Na_2CO_3 + 3OH_2 = 2ZnCO_3,3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2.$$

A large excess of ammonium salts prevents this.

On ignition this carbonate leaves ZnO, zinc oxide, also known in commerce under the name of zinc white.

Ammonium carbonate produces the same precipitate, soluble, however, in excess.

KCy gives a white precipitate of zinc cyanide, $ZnCy_2$, soluble in excess, not reprecipitated by $(NH_4)_2S$, but completely precipitated by sodium or potassium sulphide, as ZnS. (Method for the separation of Zn from Ni.)

Metallic zinc precipitates less electro-positive metals from their solutions, viz., As, Sb, Sn, Cd, Cu, Pb, Ag, Bi, Hg, and on dissolving impure metallic zinc in dilute acids (hydrochloric or sulphuric), these metals do not dissolve, as long as any zinc remains undissolved. Hence zinc protects other metals, such as copper, iron (galvanised iron), &c., from the oxidising action of air, water, and acids.

Zinc, when placed in contact with platinum, iron, &c., dissolves in alkaline solutions in the cold. (See Experiments, *ante*.)

Zinc vapour decomposes CO_2 at a high temperature, and forms ZnO and CO; ZnO however yields its oxygen to carbon. (Method of extracting metallic zinc from its ores.*)

IRON, Fe″, iv, and vi.—Occurs very abundantly in nature, mostly in a state of combination with oxygen and sulphur. It is also found as "meteoric iron" and in some very old rocks also metallic.

* It is just possible that in the extraction of zinc from ZnO that the large excess of CO present in the retort may really do most of the reduction.

There are a great number of iron minerals known, but it will suffice if those iron ores which contain the metal in sufficient quantities, and sufficiently pure and free from P, As, S, &c., to render them suitable for the extraction of iron, are mentioned. The most important are:

1st. Ores containing ferrous oxide: spathic or sparry iron ores, $FeCO_3$, containing varying quantities of $MnCO_3$, $MgCO_3$, and $CaCO_3$; black band or carbonaceous iron ore, containing from 20 to 25 per cent. of bituminous matter; clay ironstone is, as its name indicates, associated with clayey matter. It is from these two ores that the greater part of the iron manufactured in this country is derived. They occur in immediate proximity to the coal measures and limestone beds—the fuel and flux employed in their reduction to the metallic state.

2nd. Ore containing ferrous and ferric oxides: viz., magnetic iron ore, Fe_3O_4.

3rd. Ores containing ferric oxide only—viz., red hæmatite (micaceous iron, oligist, specular iron, or iron glance), Fe_2O_3. This oxide forms different hydrates which, according to the amount of water they contain, have received different names—viz., turgite, $2\ Fe_2O_3,OH_2$; needle iron ore, brown iron ore, or pyrrhosiderite, Fe_2O_3,OH_2; limonite or compact brown iron ore, brown hæmatite, $2Fe_2O_3,3OH_2$; varieties: oolitic iron ore (pea ore); yellow iron ore or xanthosiderite, $Fe_2O_3.2OH_2$.

A few other iron ores deserve attention. They are not used for the extraction of iron, but are valuable as a cheap source of sulphur —viz., iron pyrites, martial pyrites or mundic, FeS_2, found abundantly in nature; copper pyrites, Fe_2S_3, Cu_2S, and magnetic pyrites, $5FeS$, Fe_2S_3 or Fe_7S_8.

Besides these ores, iron is found in nature in combination with arsenic and sulphur, in mispickel, $FeAs_2,FeS_2$; with chromium as chrome iron ore, FeO,Cr_2O_3; with silica as chloropal, $Fe_2(SiO_3)_3,3H_2O$, and many other silicates; as sulphate, in green copperas or green vitriol, $FeSO_4,7OH_2$; as phosphate in vivianite,* $Fe_3P_2O_8,8OH_2$ (ferrous phosphate); as arsenate, in scorodite, $Fe_2As_2O_8$, and others.

All the oxides of iron part readily with their oxygen when heated with carbon, carbon monoxide or hydrogen.

Pure metallic iron is silver-white on a fresh surface, which is very permanent in dry air, but rapidly changes, by oxidation, in moist air. Its atomic weight is 55·88. Specific gravity, 7·86. Melting point of iron is given by Pictet as 1600° C., by Carnelly as 1804° C., both doubtful. Varieties of iron, as cast iron, steel, &c., melt at a much lower temperature; from 1050 to 1400° C. All varieties, wrought iron, cast irons, steel, and some alloys are eminently magnetic.

It combines directly and easily with O, S, P, As and Cl, and forms alloys with nearly all other metals, but few are used technically.

* Contains also ferric phosphate, $Fe_2P_2O_8.8OH_2$, to which the blue colour of the mineral is due.

EXPERIMENTS.

I. On heating in the tube, a clean and bright surface of iron or steel changes through many colours, becoming, finally, black, rough, and sometimes blistered. Heated to redness, black scales form, which easily detach and become reddish when exposed to damp or when rubbed. $= Fe_3O_4$. Steel is a little slower than iron in showing these changes.

II. Ordinary iron or steel placed in ordinary water rusts more or less rapidly. Water containing CO_2 or H_2O_2 acts most rapidly. Steam passed over heated iron or steel oxidises the metal, rapidly producing a black or red coating of oxide, depending on the temperature.

III. Iron or steel filings heated with sulphur: combination takes place readily, FeS being produced. It is not fusible in an ordinary tube; insoluble in water, but giving off SH_2 with HCl, or dilute H_2SO_4 "

IV. Many acids dissolve iron. HCl dissolves wrought iron more easily than cast irons or steel. The hydrogen given off has a strong odour of hydrocarbons (of the C_nH_{2n} and $C_nH_{2n}-2$ series). Pure iron gives a clear, very light green solution, from which crystals of $FeCl_2$ can be obtained. Cast irons and steels leave a greater or less amount of black residue (carbon and graphite).

H_2SO_4, dilute, behaves similarly, producing $FeSO_4$.

Nitric, moderately dilute, acts violently; red gases are evolved, and a red or green solution of ferric or ferrous nitrate formed, depending on amount and strength of the acid used. With steels the solution is generally *brown* owing to the combined carbon being acted upon and dissolved.

Irons and steel may be placed in very strong nitric acid without any action being apparent. (This is the so-called passive state.) On being touched, under the acid, with a metal, like Zn, or scratched, an action will generally commence. There are several (attempted) explanations. One is that a very fine film of insoluble oxide forms and acts as a protective layer; scratching or touching with a more positive metal removes or reduces this and lets the action commence and spread over the whole surface.

V. Alkalies, including ammonia, have no action either on metallic iron or its oxides. Bright steel or iron is not affected by any alkaline oxidising solutions at ordinary temperatures.

The red oxide produced in I. or II. ($= Fe_2O_3$) dissolves in HCl and H_2SO_4, giving red solutions which do not easily crystallise = Ferric salts.

DRY REACTIONS.

✓ On heating the different iron compounds on charcoal before the blowpipe, they leave a black magnetic residue; when heated in the outer flame on a borax bead iron compounds impart a dark red colour to the borax whilst hot, becoming light yellow when cold. In the reducing flame they give an olive-green to bottle-green bead.

The reactions with microcosmic salts are similar but less distinct. The presence of Co, Cu, Ni, Cr, conceals the colour of the iron bead. Ferric sulphides and arsenides must be roasted, previous to being introduced into the borax bead. When heated with Na_2CO_3 on charcoal, in the reducing flame, metallic iron is obtained as a black magnetic powder.

REACTIONS IN SOLUTION.

Iron forms two series of salts—viz., ferrous and ferric salts. The metal dissolves readily in dilute acids, such as HCl, H_2SO_4, forming

ferrous salts, $FeCl_2$, $FeSO_4$, with evolution of hydrogen. Cold very dilute nitric acid dissolves finely divided iron (iron filings) without evolving hydrogen gas, the nitric acid being decomposed, so as to form ferrous nitrate and ammonium nitrate; the reaction may be expressed thus:

$$4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3OH_2.$$

The metal iron exists in all these salts in the dyad condition, but exhibits a marked tendency to pass into a higher stage. Exposed to the air, solutions of $FeCl_2$ and $FeSO_4$ absorb oxygen, and are gradually converted into ferric salts. The same change is produced by the action of various oxidising agents, such as Cl, Br, I, ClNaO, $KClO_3$ and in the presence of HCl by HNO_3, $AgNO_3$, $AuCl_3$, $K_2Mn_2O_8$, K_2CrO_4, and others. Ferrous compounds are, therefore, powerful *reducing* agents, and are frequently employed as such.

A. *Ferrous compounds.**—Ferrous sulphate or chloride is soluble and well adapted for reactions. Ferrous salts are mostly green when hydrated and white when anhydrous.

$(NH_4)_2S$ (group-reagent) gives a black precipitate of ferrous sulphide, FeS, insoluble in alkalies and alkaline sulphides, easily decomposed and dissolved by dilute hydrochloric acid, with evolution of sulphuretted hydrogen. The moist precipitate absorbs oxygen from the air, and is rapidly converted into ferrous sulphate, and lastly into yellow basic ferric sulphate, with evolution of much heat. (This oxidation constitutes a frequent cause of the spontaneous inflammation of pyritical coal (which contains Fe_7S_8) in mines and on board vessels).

SH_2 does not precipitate neutral or acid solutions of ferrous salts; ferrous acetate even is only partially precipitated.

Alkaline hydrates and ammonia, also CaH_2O_2 and BaH_2O_2, precipitate from ferrous salts (free from ferric salts) white ferrous hydrate, $Fe(HO)_2$, which turns rapidly to a dirty green colour, and ultimately becomes reddish-brown, owing to absorption of oxygen from the atmosphere. Ammonium salts partially prevent the precipitation by the fixed alkalies, and ammonium hydrate gives but a slight precipitate in a ferrous solution, containing a considerable amount of ammonium chloride. The presence of non-volatile organic acids, of sugar, &c., also prevents the precipitation more or less.

Soluble carbonates precipitate white ferrous carbonate, $FeCO_3$, which becomes rapidly oxidised when exposed to air.

$K_4Fe(CN)_6$ (potassium ferrocyanide) produces, by the replacement

* **Ferrous sulphate forms a number of so-called double sulphates, with the alkali metal sulphates and ammonium sulphate. $FeSO_4(NH_4)_2SO_4,6H_2O$ is much used in volumetric work, as it is easily obtained very pure, and contains almost exactly one-seventh of its weight of iron.**

of K_2 by Fe, a bluish-white precipitate of potassium ferrous ferrocyanide, $K_2Fe''Fe(CN)_6$, thus:

$$FeSO_4 + K_4Fe(CN)_6 = \underset{\text{Bluish-white precipitate *}}{K_2Fe''Fe(CN)_6} + K_2SO_4,$$

insoluble in dilute hydrochloric acid. The light blue precipitate is rapidly converted into a dark blue precipitate, or Prussian blue, either by exposure to the air, or more speedily by an oxidising agent (in solution), thus:

$$4K_2Fe''Fe(CN)_6 + 2Cl_2 = \underset{\text{Prussian blue *}}{Fe_4(Fe(CN)_6)_3} + 4KCl + K_4Fe(CN)_6,$$

$K_6Fe_2(CN)_{12}$ † (potassium ferricyanide) produces a dark blue precipitate of ferrous ferricyanide, $Fe_3Fe_2(CN)_{12}$ (Turnbull's blue), insoluble in hydrochloric acid, thus:

$$3FeSO_4 + K_6Fe_2Cy_{12} = \underset{\text{Turnbull's blue *}}{Fe''_3Fe'''_2Cy_{12}} + 3K_2SO_4.$$

NaHO or KHO decomposes both precipitates with formation of soluble alkaline ferro- and ferri-cyanides, and separation of ferrous and ferric hydrates, thus:

$$(1)\ K_2Fe''FeCy_6 + 2KHO = K_4FeCy_6 + Fe(HO)_2;$$
$$(2)\ Fe_4(FeCy_6)_3 + 12NaHO = 3Na_4FeCy_6 + 2Fe_2(HO)_6;$$
$$(3)\ Fe'''_3Fe'''_2Cy_{12} + 6NaHO = Na_6Fe_2Cy_{12} + 3Fe(HO)_2.$$

N.B.—Cy is the abbreviation for (CN), the cyanogen radicle. The molecule of cyanogen is C_2N_2.

NH_4SCN (ammonium sulphocyanate) gives no coloration, if the ferrous solution contain no ferric salt, but the test is very delicate and most generally sufficient ferric salt is present to give a faint red coloration.

B. *Ferric compounds.*—A solution of ferric chloride, Fe_2Cl_6,‡ may be used.

$(NH_4)_2S$ (group-reagent) produces a black precipitate of ferrous sulphide, FeS, *mixed with sulphur*, thus:

$$Fe_2Cl_6 + 3(NH_4)_2S = 2FeS + S + 6NH_4Cl.$$

Dilute solutions of iron give only a greenish coloration.

On dissolving the black precipitate in dilute hydrochloric acid, sulphuretted hydrogen is evolved, and white insoluble sulphur is

* These precipitates cannot form, therefore, in an alkaline solution.

† This may be written K_3FeCy_6.

‡ This formula, Fe_2Cl_6, may be considered as "convenient," and is retained for that reason only. $FeCl_3$ is, no doubt, the real constitutional formula, as indicated by the vapour density of the anhydrous salt.

left. (Distinction between ferrous and ferric salts.) Ferric sulphide cannot be formed in the wet way; native sulphides exist, however—viz., FeS_2 and Fe_2S_3—which are insoluble in dilute hydrochloric acid, but dissolve with evolution of SH_2 when in contact with metallic zinc.

SH_2 does not precipitate Fe_2Cl_6; its hydrogen acts as a reducing agent upon the ferric salt, converting it into $2FeCl_2$ and $2HCl$, *white sulphur* being precipitated, which renders the solution of the ferrous salt milky.

Alkaline hydrates and ammonia, also calcium or barium hydrates, precipitate the reddish-brown ferric hydrate, $Fe_2O_3,2OH_2$, insoluble in excess and in ammonium salts (excepting the carbonate). Non-volatile organic bodies (*e.g.*, tartaric or citric acid, sugar, &c.) prevent its precipitation by ammonium hydrate, but not by ammonium sulphide. The precipitate retains with great tenacity small portions of the fixed alkalies.

Na_2CO_3 and K_2CO_3 produce the same precipitate with evolution of carbonic anhydride.

HNa_2PO_4 (hydrogen disodium phosphate) produces a yellowish-white flocculent gelatinous precipitate of ferric phosphate, $Fe_2P_2O_8 + 4OH_2$. The precipitation is complete only in the presence of an alkaline acetate, thus:

$$Fe_2Cl_6 + 2Na_2HPO_4 + 2CH_3CO_2Na = Fe_2P_2O_8 + 6NaCl + 2CH_3CO_2H.$$

On the addition of the first few drops of hydrogen disodium phosphate, and as long as the ferric salt is largely in excess, the precipitate may disappear again, especially on gently warming, since it is somewhat soluble in ferric acetate. When the precipitation is nearly complete, the ferric phosphate separates more speedily, especially on stirring and gently heating, and allowing to subside after each addition of the phosphate solution. The precipitated ferric phosphate should be filtered hot, and washed by decantation with hot water. It is soluble in dilute mineral acids—hence the addition of an alkaline acetate; insoluble, however, in acetic acid (like the corresponding chromic * and aluminic phosphates).

Phosphates of the alkaline earthy metals (Ba, Sr, Ca, Mg), which are readily soluble in acetic acid, may thus be separated by filtration from the phosphates of Fe^{iv}, Al^{iv} (and Cr^{iv}). Owing to this property of ferric phosphate, it is also possible to decompose alkaline earthy phosphates in a solution containing an excess of sodium acetate, by adding, drop by drop, a neutral solution of ferric chloride, according to the equation:—

$$2BaHPO_4 + 2CH_3CO_2Na + Fe_2Cl_6 = Fe_2P_2O_8 + 2BaCl_2 + 2NaCl + 2CH_3CO_2H.$$

* Chromic phosphate, especially when freshly precipitated, is dissolved, although with some difficulty, in acetic acid, especially on heating.

The ferric chloride must be added as long as a yellowish-white precipitate comes down, and till the supernatant liquid becomes just red, from the formation of ferric acetate.

Ferric phosphate dissolves in excess of hydrogen disodium phosphate in the presence of ammonium hydrate or carbonate, to a brownish-red solution. It is somewhat soluble in ferric, but not in ferrous, acetate. Ammonium hydrate reduces it to a basic phosphate. Potassium or sodium hydrate removes nearly the whole of the acid. Fusion with caustic fixed alkalies, or with fusion-mixture, or boiling with ammonium sulphide, decomposes ferric phosphate completely, leaving the iron as oxide or sulphide, from which the soluble alkaline phosphate can be separated readily by filtration.

Citric or tartaric acid prevents the precipitation of ferric phosphate from solutions.

K_4FeCy_6 gives a fine blue precipitate, $Fe_4(FeCy_6)_3$, known as Prussian blue, thus:—$2Fe_2Cl_6 + 3K_4FeCy_6 = Fe_4(FeCy_6)_3 + 12KCl$. Insoluble in hydrochloric acid; decomposed by KHO or NaHO; soluble in oxalic acid and also in excess of K_4FeCy_6, to a blue solution.

$K_6Fe_2Cy_{12}$ produces no precipitate, but the yellow colour of the ferric solution changes to reddish-brown. (Distinction between ferrous and ferric salts.)

NH_4SCN (ammonium sulphocyanate) gives a dark-red or blood-red colour, even in the case of very dilute solutions, which is not destroyed by hydrochloric acid. The sensitiveness of the reaction is heightened by shaking a hydrochloric acid solution, to which the sulphocyanate has been added, with ether. The blood-red ferric sulphocyanate, $Fe_2(SCy)_6$, being soluble in ether, becomes thus concentrated into a small bulk of liquid. Very small amounts of iron can be detected by this means. The colour of the liquid is readily destroyed by a solution of mercuric chloride (also by tartaric or phosphoric acid). (Distinction of Fe'' from Fe^{iv}.)

Excess of sodium acetate, added to a solution of ferric salt, produces a deep-red coloured liquid, owing to the formation of ferric acetate. On diluting and boiling, the whole of the iron is precipitated as basic ferric acetate in the form of brownish-yellow flakes, which should be filtered hot and as quickly as possible when the fluid has become clear. (Method of separating Fe^{iv} from Mn''.)

Ammonium succinate or benzoate precipitates ferric, but not ferrous, salts, as ferric succinate or benzoate.* The ferric solution should be perfectly neutral. Salts of Mn, Co, Ni, Zn, are not precipitated. (Method of separation of Fe^{iv} from Fe'', Mn, Ni, Co, Zn.)

Freshly precipitated and well washed barium or calcium carbonate, suspended in water, precipitates ferric (not ferrous) chloride, as ferric hydrate, $Fe_2(HO)_6$, mixed with basic salt, with evolution of

* The formulæ of these compounds will be explained under the respective acids.

carbonic anhydride. The reagent is added to the neutral ferric salt in the cold, and well shaken up with it till the reddish-brown precipitate acquires a whitish appearance, from excess of the alkaline earthy carbonate.

Barium carbonate separates in like manner the higher or -ic chlorides of this group from the lower or -ous chlorides. In order to separate ferric from ferrous compounds, or ferric, chromic, and aluminic compounds from ferrous, zinc, manganous, cobaltous, and nickelous salts, it is necessary that these metals should all be obtained in the form of chlorides. On the addition of barium carbonate, the respective hydrates, mixed with basic salts, are precipitated from the ferric, chromic and aluminic chlorides, whilst ferrous chloride and the chlorides of Zn, Mn, Ni, and Co are not affected. Air has to be excluded as carefully as possible, in order to prevent the oxidation of the ferrous, manganous and cobaltous hydrates during the operation. The reaction should be performed in a small flask, filled nearly to the neck with the liquid, and kept well corked, after the evolution of the carbonic anhydride has ceased. The addition of ammonium chloride, previous to the precipitation with barium carbonate, almost entirely prevents *any* cobaltous or nickelous hydrates from falling out with the barium carbonate precipitate. (Method for separating Fe^{iv} (also Al and Cr) from Fe'', Zn'', Mn'', Ni'', and Co''.)

The precipitate is filtered off, and dissolved in hydrochloric acid; the barium removed by means of dilute sulphuric acid, and the Fe, Cr and Al, precipitated by ammonium hydrate.

Tannic as well as gallic acid (tincture of nut-galls) produces from neutral ferric salts a bluish-black precipitate (ink) readily soluble with decomposition in acids.

Ferric salts can act as oxidising agents in some cases. Thus H_2SO_3 is converted into H_2SO_4; KI gives off iodine; $Sn''Cl_2$ is converted into $Sn^{iv}Cl_4$; $Na_2S_2O_3$; (sodium hyposulphite) is oxidised to $HNaSO_4$. It is generally necessary for an acid to be present. Iron, zinc, or magnesium readily reduce ferric to ferrous salts.

C., Ferric anhydride, FeO_3, or ferric acid, H_2FeO_4, containing hexad iron, has never been obtained in an uncombined state. The alkali salts only are known, and are obtained by fusing ferric oxide with nitre. Ferrates are decomposed far more readily than manganates.

CHROMIUM, Cr'', ^{iv}, and ^{vi}. The element is not employed in the metallic state, but is used as an alloy with iron. Chrome steel is such an alloy. It is extremely hard even without the process of hardening. It is generally formed by heating steel for some time to a very high temperature with chrome iron ore in a strongly reducing atmosphere or in contact with carbon. Little is known of its physical properties in a separate state. Its atomic weight = 52·45, specific gravity 6·50. Its melting point is not known with certainty, but is higher than that of platinum. As obtained by reduction of the chloride, with sodium or magnesium, metallic chromium is very

hard, crystalline, and about the colour of iron. It oxidises slowly in air, and dissolves readily in acids with the exception of strong nitric, towards which it behaves like iron. This element is not very widely distributed. It occurs in nature chiefly as chrome iron ore, Cr_2O_3FeO, and crocoisite, $PbCrO_4$. Chromic oxide constitutes the colouring matter in ruby, green serpentine, &c. Many of its compounds are employed as colours.

EXPERIMENTS.

I. Ferro-chrome or chrome-steel, on heating in the open tube, shows little change.

II. Heated very strongly with sulphur, a little FeS is formed.

III. Acids dissolve it very slowly. The more Cr the slower the action. Strong nitric is the best solvent. On evaporating to dryness in a small dish, adding a little (solid) KNO_3 potassium nitrate, and fusing a mass consisting of Fe_2O_3, and K_2CrO_4 is left. Water dissolves the K_2CrO_4, giving a yellow solution.

IV. Ferro-chrome or other alloy will also give K_2CrO_4, on direct fusion with KNO_3; better with Na_2O_2 and KNO_3.

Most compounds are made from chrome iron ore, $FeCrO_4$, by fusion with alkalies and decomposition of the alkaline chromate formed.

I. Chromium oxide, Cr_2O_3, heated alone does not change. Acids dissolve it, forming green salts. The sulphate, Cr_23SO_4, is a green-purple crystalline body. The chloride is very deliquescent, like the ferric chloride.

II. The oxide scarcely changes on heating with sulphur.

III. Ammonia does not dissolve it, but strong NaHO solution does the precipitated oxide. After intense ignition the oxide is nearly unaffected. All alkalies and alkaline carbonates, also CaO, give chromates on fusion with the oxide; they are yellow, crystalline and soluble.

DRY REACTIONS.

✓ Chromium compounds are readily recognised by the very characteristic green colour which the oxide imparts to borax and microcosmic salt, especially in the reducing flame. Finely powdered chrome iron ore, or other very insoluble and difficultly decomposable chromium compounds, fused for a few minutes in a platinum spoon or crucible with four times its weight of hydrogen potassium sulphate, and then again with the addition of an equal bulk of nitre and potassium carbonate (equally mixed), yields a yellow mass of potassium chromate, K_2CrO_4, which is soluble in water to a yellow solution. If manganese were present, the solution would be green, owing to the formation of potassium manganate. This latter can be readily removed by adding a few drops of alcohol to the solution, heating and filtering off the manganic hydrate. The chromate remains unchanged in the alkaline solution.

REACTIONS IN SOLUTION.

Chromic salts can be prepared from the yellow K_2CrO_4, or the red potassium dichromate, $K_2Cr_2O_7$, by heating with strong hydro-

chloric acid and adding alcohol, when the yellow solution changes to a deep green solution of Cr_2Cl_6.*

Chromium is capable of forming at least three series of compounds—

Chromous compounds.	Chromic compounds.	Chromates.
$Cr''Cl_2$.	$'Cr'''_2Cl_6$.	K_2CrO_4.
$Cr''O$.	$'Cr'''_2O_3$.	$PbCrO_4$.
$Cr''(HO)_2$.	$'Cr'''_2(HO)_6$.	&c.,
&c.	&c.	

of which the two latter are best known.

A. *Chromic Compounds.*—The sulphate or double sulphate with K or Na (CrAlum), chloride, nitrate, or acetate, are soluble and easily obtained salts.

$(NH_4)_2S$ (group-reagent) precipitates bluish-green chromic hydrate, $Cr_2(HO)_6$, insoluble in excess.

NH_4OH precipitates the hydrate, somewhat soluble in excess, the fluid acquiring a pink tint. This is probably due to a chrome ammonium compound. On boiling for a few minutes the precipitation is generally complete.

KHO or NaHO, same precipitate, readily soluble in excess of the cold reagent to a green solution; reprecipitated by long-continued boiling, or on adding NH_4Cl, whereby the fixed alkali is removed as KCl or NaCl, with liberation of ammonia.

Na_2CO_3 or K_2CO_3 gives a greenish precipitate of basic carbonate (varying in composition), somewhat soluble in excess.

HNa_2PO_4 (hydrogen disodium phosphate) precipitates green chromic phosphate, $Cr_2P_2O_8$, soluble in mineral acids, difficultly soluble in acetic acid.

Barium carbonate precipitates a basic carbonate. The precipitation takes place in the cold, but is completed only after long digestion —two or three days.

In the presence of citric, tartaric, and oxalic acid, and also of sugar, the precipitation of chromic salts by means of ammonia, sodium or barium carbonate, is more or less incomplete.

Chromic compounds may be recognised also by converting the chromic oxide into chromic acid. This may be accomplished—

1st. By boiling a solution of Cr_2Cl_6 with PbO_2 and KHO or NaHO. The reaction which takes place, and which is indicated by a change of colour (from green to yellow) may be expressed thus:

$$(1)\ Cr_2Cl_6 + 6KHO = \underset{\substack{\text{Soluble in}\\ \text{excess of KHO}}}{Cr_2(HO)_6} + 6KCl;$$

$$(2)\ Cr_2(HO)_6 + 3PbO_2 = \underset{\substack{\text{Soluble in}\\ \text{KHO}}}{2PbCrO_4} + \underset{\substack{\text{Soluble in}\\ \text{KHO}}}{PbO} + 3OH_2.$$

* This is most probably $CrCl_3$.

On acidulating the solution with acetic acid a precipitate of lead chromate, $PbCrO_4$, is obtained.

2nd. By boiling a solution of Cr_2Cl_6 with NaHO and sodium hypochlorite, ClNaO, or bleaching powder, $CaOCl_2$, thus:

$$Cr_2(HO)_6 + 3ClNaO + 4NaHO = \underset{\text{Yellow sodium chromate}}{2Na_2CrO_4} + 3NaCl + 5OH_2.$$

3rd. By fusion with alkaline carbonates and nitre on platinum foil.

B. Chromic anhydride, CrO_3, combines with water to form chromic acid, H_2CrO_4. This forms with monad metals two classes of salts, the normal or yellow chromates, viz., *e.g.*, K_2CrO_4, and the dichromates, *e.g.*, $K_2Cr_2O_7$, isomorphous with the corresponding sulphates and disulphates. A solution of the neutral potassium chromate is changed to an orange-red (acid) dichromate solution on the addition of an acid, thus:

$$2K_2CrO_4 + 2HCl = K_2Cr_2O_7 + 2KCl + OH_2.$$

Conversely, the dichromate is transformed into a chromate on the addition of an alkali, thus:

$$2K_2Cr_2O_7 + 2KHO = 2K_2CrO_4 + OH_2.$$

Trichromates, and even higher stages, are also known, and may be easily obtained by treating an alkaline or other chromate with nitric acid, which removes some of the positive metal. They are less soluble than the normal salts, and more intensely coloured, and generally crystallise well.

Chromic anhydride may be prepared by slowly adding to a cold saturated solution of the red potassium dichromate 1½ times its bulk of concentrated sulphuric acid, and allowing it to cool slowly. CrO_3 crystallises out in brilliant crimson-red prisms. The mother-liquor is poured off, and the crystals placed to drain upon a porous tile or slab of unglazed porcelain (biscuit ware), or in a funnel which has been lightly plugged with asbestos. They must be protected from moist air, as the substance is extremely hygroscopic.

Chromic anhydride is one of the most powerful oxidising agents known. Four molecules of CrO_3 yield upon ignition chromic oxide and three molecules of oxygen, according to the equation:

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

Reactions of CrO_3 based upon its Oxidising Action.

A solution of potassium dichromate, $K_2Cr_2O_7$, will show these.

SH_2, in the presence of free hydrochloric acid, reduces the

orange-red solution to a green liquid, sulphur being precipitated, thus:

$$K_2Cr_2O_7 + 8HCl + 3SH_2 = Cr_2Cl_6 + 2KCl + 7OH_2 + S_3.$$

A little H_2SO_4 is generally formed.

$(NH_4)_2S$, added in excess to a solution of an alkaline chromate or dichromate, precipitates dirty green hydrated chromic chromate. On boiling, the whole of the chromium separates as green chromic hydrate, thus:

$$^{*}K_2Cr_2O_7 + 3(NH_4)_2S + 7OH_2 = Cr_2(HO)_6 + S_3 + 2KHO + 6NH_4OH.$$

H_2SO_3, in the presence of a little free acid, reduces potassium dichromate to chromic sulphate, thus:

$$K_2Cr_2O_7 + 3H_2SO_3 + H_2SO_4 = Cr_2(SO_4)_3 + K_2SO_4 + 4OH_2.$$

Chromic sulphate and potassium sulphate constitute potassium chrom-alum, $K_2Cr_2(SO_4)_4$.

$H_2C_2O_4$ (oxalic acid), in the presence of free acid (dilute sulphuric), produces the same reduction, carbonic anhydride being evolved. Six molecules of CO_2, or three of oxalic acid, are the measure for one molecule of potassium dichromate.

$$K_2Cr_2O_7 + 3H_2C_2O_4 + 4H_2SO_4 = K_2Cr_2(SO_4)_4 + 6CO_2 + 7OH_2.$$

Hot concentrated sulphuric acid decomposes the dichromate, with evolution of oxygen and formation of potassium chrom-alum, thus:

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2Cr_2(SO_4)_4 + 8H_2O + 3O_2.$$

HCl (concentrated) evolves chlorine, and the hydrogen combines with the three available atoms of oxygen in the dichromate thus:

$$K_2Cr_2O_7 + 14HCl = Cr_2Cl_6 + 2KCl + 7OH_2 + 3Cl_2.$$

H_3AsO_3, arsenious acid (in a hydrochloric acid solution), is converted into H_3AsO_4, thus:

$$K_2Cr_2O_7 + 3H_3AsO_3 + 8HCl = Cr_2Cl_6 + 2KCl + 3H_3AsO_4 + 4OH_2.$$

$SnCl_2$, $SbCl_3$, $FeCl_2$, Zn (Fe, Sn, &c.) in the presence of dilute HCl, reduce also chromates or dichromates. The reduction is quite

* The action is much more complex than here given, some of the S becoming oxidised to SO_3, which combines with the ammonia, forming $(NH_4)_2SO_4$. The amount of S oxidised is generally about a third of that represented as liberated in the above equation. On heating NH_3 escapes, sulphide and sulphate of potassium being left in solution.

√ KHO or NaHO* precipitates the hydrate, readily soluble in excess, forming a saline compound, sodium aluminate, $Al_2Na_6O_6$, which is reprecipitated by excess of ammonium chloride, or by ammonia after neutralisation of the alkali by hydrochloric acid. The alkaline solution is not precipitated by ammonium sulphide. (Method of separation of Al from Fe^{iv}.)

NH_4OH precipitates the hydrate, somewhat soluble in excess, insoluble in the presence of much ammonium chloride, and on boiling.

Na_2CO_3 or K_2CO_3 precipitates basic carbonate of uncertain composition.

$BaCO_3$ precipitates $Al_2(HO)_6$, slowly, but completely, even in the cold, mixed with a basic salt. Carbonic anhydride escapes.

HNa_2PO_4 gives a bulky white precipitate of aluminic phosphate, $Al_2P_2O_8$, insoluble in ammonium hydrate and chloride; soluble in KHO or NaHO, like the hydrate, and in acids, but not in hot acetic acid. (Distinction of Al_2O_3 from aluminic phosphate.) Alkaline acetates precipitate $Al_2P_2O_8$ from its solution in mineral acids. The presence of citric acid, but not of tartaric acid or of sugar, prevents its precipitation. NH_4Cl precipitates the phosphate from its soda solution.

In order to decompose aluminic phosphate (as in the mineral wavellite) it is best to fuse the finely powdered mineral with 1½ parts of finely divided SiO_2, and 6 parts of Na_2CO_3, in a platinum crucible for about half an hour. The mass is digested for some time with water, and acid ammonium carbonate NH_4HCO_3 added in excess; it is then filtered and washed. The residue consists of aluminic and sodium silicates, the solution contains the sodium phosphate. Dissolve the residue by dilute hydrochloric acid, and evaporate to dryness to separate the silica and filter. The filtrate may be tested for Al in the usual way.

Alumina occurs mostly in minerals which are not soluble in acids. Boiling with concentrated sulphuric acid attacks many; all are, however, decomposed by fusion with $KHSO_4$, or with fusion mixture, after which they are soluble either in water or in dilute hydrochloric acid.

Powder up some porcelain very finely, and fuse for half an hour in a platinum crucible, with four times its weight of fusion mixture. Extract with water. Transfer both the soluble and insoluble portion —consisting of alkaline aluminate—to a porcelain dish, acidulate with hydrochloric acid, and evaporate to dryness. Take up with a few drops of concentrated hydrochloric acid and hot water, and filter; wash the insoluble SiO_2 well with hot water. The filtrate contains the aluminium as chloride, from which it can be precipitated by ammonia as usual.

* Potassium and sodium hydrates are mostly contaminated with alumina, derived during the manufacture from porcelain vessels, and it is therefore necessary to employ pure NaHO (prepared in silver or nickel vessels) for the separation of Fe and Al. It must also be recollected that NaHO acts, in the course of an ordinary analysis, destructively upon porcelain and glass vessels, dissolving both silica and alumina which give similar reactions with ammonia and its salts.

Aluminic silicate is often found in nature associated with potassium or sodium silicate, as in felspar and albite. In order to test for potassium and sodium, alkali salts must, of course, be carefully avoided. This can be done by making use of hydrofluoric acid, or by heating in a platinum crucible or on foil with CaO or with calcite, $CaCO_3$.

Introduce a small quantity of finely powdered felspar into a platinum * crucible or dish; cover with liquid hydrofluoric acid, and evaporate at a gentle heat in a closet or under a hood which is connected with the chimney. HF attacks the SiO_2, forming silicon fluoride, SiF_4—a volatile compound—and leaves the aluminium and potassium behind as fluorides which dissolve in dilute hydrochloric acid:

$$K_2Al_2Si_6O_{16} + 32HF = \underset{\text{Volatile}}{6SiF_4} + 2KF + Al_2F_6 + 16OH_2.$$

The decomposition is generally only completed after two or three evaporations with HF.

Mix the fine powder of felspar with either powdered calcite or CaO and heat strongly, best in a covered crucible, for thirty minutes. On treating with HCl and evaporating to dryness the SiO_2 becomes insoluble and Al, Ca, K may be taken up by water as chlorides.

N.B.—The separation of the metals of Group III. is surrounded by some difficulties which arise from the possible simultaneous precipitation of

1st. Sulphides, NiS, CoS, MnS, ZnS, FeS,
2nd. Hydrates, $Cr_2(HO)_6$, $Al_2(HO)_6$, and
3rd. Phosphates of Cr, Al, Ba, Sr, Ca, Mg,

and it is therefore well always to ascertain, by a special experiment whether phosphoric acid is present or not in the solution under examination.

This can readily be done by adding to a small part of the solution a little concentrated nitric acid, and a solution of ammonium molybdate,† a yellow precipitate is obtained especially on gently heating, showing the presence of phosphoric acid. If no precipitate is obtained, phosphates are absent.

(*a*) *Phosphoric acid is absent.*—This is indicated if the original substance dissolved readily in water. If insoluble in water, but soluble in dilute acids, phosphoric acid may likewise be absent from the substance.

It would appear at first sight that the deportment of the five sulphides and two hydrates with ammonium chloride and ammonium hydrate, sodium or potassium hydrate, or dilute acids (*e.g.*, HCl),

* With care a leaden dish will do.
† For the preparation of this reagent see Appendix Reagents.

would enable the members of this group to be separated, or several of them, from each other. It has been shown, for example, that—

1st. Ni,Co,Mn,Zn are not precipitated by ammonia from a hot solution containing large excess of NH_4Cl; whilst $Fe_2(HO)_6$,$Cr_2(HO)_6$, and $Al_2(HO)_6$ are precipitated. It has, however, been found that the mode of separation, based upon this solvent property of ammonium chloride, gives but imperfect results, since the $Fe_2(HO)_6$ carries down varying quantities of other oxides, especially on exposure of the solution to the air, when higher oxides of manganese and cobalt are formed, which are not soluble in ammonium chloride. Small quantities of Ni, Co, Mn, and Zn may thus be overlooked altogether. It is only by redissolving the precipitate and reprecipitating several times over with ammonium chloride and ammonia, as long as the ammoniacal filtrate gives a precipitate with sulphuretted hydrogen, that iron can be completely separated from manganese, &c., in this manner.

With these precautions, however, it is mostly possible to separate the metals of this group from each other by first precipitating ferric, chromic, and aluminic hydrates by means of NH_4Cl and NH_4OH, and then from the filtrate, the sulphides of Ni, Co, Mn, and Zn by means of SH_2 or $(NH_4)_2S$.

2nd. That Zn, Al and Cr are precipitated by KHO or NaHO, but are soluble in excess, whilst the other metallic hydrates are insoluble. From this it would appear that these three metals can be separated by means of the fixed alkaline hydrates. But it has been found here again that $Fe_2(HO)_6$, $Ni(HO)_2$, $Co(HO)_2$, $Mn(HO)_2$ carry down appreciable quantities of $Zn(HO)_2$ and more especially the $Fe_2(HO)_6$ precipitate of $Cr_2(HO)_6$, and that a complete separation cannot be effected by precipitation with KHO or NaHO.

3rd. Cold dilute hydrochloric acid does not dissolve CoS or NiS to any great extent, but dissolves the other sulphides and hydrates. This method, if practised with care, gives good results, small traces only of CoS and NiS being generally dissolved out. But as it leaves the iron, aluminium, and chromium still to be separated from manganese and zinc, no saving of labour is effected thereby in the separation of these seven metals.

Finely divided freshly precipitated baric carbonate is a reagent which separates the lower oxides—viz., ZnO, MnO, NiO, CoO (this latter not quite so perfectly, except in the presence of much ammonium chloride), from the higher oxides—viz., Fe_2O_3, Al_2O_3, and Cr_2O_3. The metals should be first obtained as chlorides.

The examination of the precipitate produced by barium carbonate is based upon—

1st. The solubility of $Al_2(HO)_6$ in sodium hydrate.

2nd. The conversion of Cr_2O_3 into CrO_3 by fusion with sodium carbonate and nitre, or by boiling with ClNaO, or with PbO_2 in an alkaline solution.

The examination of the filtrate is based upon—

1st. The solubility of $Zn(HO)_2$ in sodium hydrate.
2nd. " MnS in acetic acid.
3rd. The formation of soluble $K_6Co_2Cy_{12}$ and the precipitation of Ni as black $Ni_2(HO)_6$ by sodium hypochlorite, or hypobromite.*

Directions for the separation of these seven metals will be found in the analytical tables under Group IIIA.

(β) *Phosphoric acid is present.*—The original substance was either insoluble or only partially soluble in water, but soluble in hydrochloric acid. In this case NH_4Cl and NH_4OH† produce a precipitate before $(NH_4)_2S$ is added. If $(NH_4)_2S$ is added without filtration after the addition of NH_4OH, the precipitate may possibly consist of NiS, CoS, MnS, ZnS, FeS, $Al_2(HO)_6$, $Cr_2(HO)_6$, as well as the phosphates of (Cr), Al, Mg, Ca, Sr, Ba.

Ammonium chloride and ammonia precipitate Ni, Co, Mn, Zn, and Fe phosphates without decomposition. Ammonium sulphide converts the phosphates of Ni, Co, Mn, Zn, and Fe into sulphides and ammonium phosphate and this could then act upon any soluble salts of Ba, Ca, Sr, Mg, and convert them into phosphates although they were not as phosphates in the original mixture.

An example will make this clear. Supposing that the substance under examination consists of barium carbonate and calcium and ferric phosphates, $BaCO_3$,$Ca_3P_2O_8$ and $Fe_2P_2O_8$. On dissolving in hydrochloric acid, barium chloride is formed, and the calcium and ferric phosphates are dissolved without decomposition. On adding NH_4Cl and NH_4OH, a yellowish-white precipitate of $Fe_2P_2O_8$ and $Ca_3P_2O_8$ is obtained, whilst $BaCl_2$ is not precipitated. On adding, however, $(NH_4)_2S$ as well as the ammonium chloride and ammonia to the solution, $Fe_2P_2O_8$ is decomposed into ferrous sulphide and ammonium phosphate, which latter, by acting upon the $BaCl_2$, would precipitate barium phosphate.

In order to avoid this, the precipitate produced in Group III. by NH_4Cl and NH_4OH, which contains for the most part the whole of the phosphates, is filtered off, and $(NH_4)_2S$ added to the filtrate only.

The precipitate produced by ammonia is dissolved in a little dilute HCl, nearly neutralised with Na_2CO_3, and an excess of a solution‡ containing sodium acetate and acetic acid is added. The phosphates of iron, chromium, and aluminium are precipitated. Any phosphates of the alkaline earths left undecomposed by the ferric chloride already present in the solution, are held in solution by the acetic acid. To the filtrate add Fe_2Cl_6, drop by drop, as long as a

* Instead of NaOCl bromine water may generally be used. In an alkaline solution a hypobromite as NaOB is formed. The oxidising action is just the same.

† If ammonium chloride and ammonia should give no precipitate, it is obvious that no phosphates and no Fe, Al and Cr need be looked for.

‡ For the preparation of this reagent see Appendix.

precipitate* is obtained, and till the colour of the supernatant liquid becomes distinctly reddish. Digest at a gentle heat: allow to subside and filter. In this manner the whole of the phosphates of the alkaline earthy bases are decomposed, with formation of the $Fe_2P_2O_8$, insoluble in acetic acid—(which precipitate may be neglected), and chlorides of Mg, Ba, Sr, Co which remain in solution, together with the chlorides of Ni, Co, Mn, Zn. The whole of the phosphoric acid having thus been removed, the metals that were originally present as phosphates may be detected in the usual way.

It may be of interest to ascertain whether oxalates of Ba, Sr and Ca (which are destroyed by evaporation with nitric acid and ignition, before proceeding to Group III.), were present in the original mixture, in which case the evaporation to dryness and ignition must be omitted.

The precipitate produced in Group III. by ammonium chloride and ammonia alone, contains the oxalates, as well as the phosphates of the alkaline earthy bases, and possibly also gelatinous silica. The oxalates are decomposed by gently igniting the precipitate, and are converted into carbonates. The ignited mass effervesces strongly on extraction with dilute hydrochloric acid. When the solution is evaporated to dryness and again taken up with dilute HCl, the silica, if present, is rendered insoluble, and may be separated by filtration. To the acid solution, which may possibly contain phosphates of Mg, Ca, Sr, and Ba, as well as chlorides of the bases, present before ignition as oxalates, add NH_4Cl and NH_4OH and filter off. The filtrate contains the chlorides of Ba, Sr and Ca, and is tested separately according to Table IV. All bases so discovered must have been present originally as oxalates.

The separation of the individual members of this group is based upon:

1st. The insolubility of the phosphates of Fe, Al (and Cr) in acetic acid in the presence of an alkaline acetate.

2nd. The separation of the whole of the phosphoric acid which is in combination with the alkaline earthy bases, by means of Fe_2Cl_6, in an acetic solution.

All other operations are identical with those already described.

Phosphates may be decomposed in another way, depending on the fact that almost all phosphates, excepting those of molybdenum and tin, are soluble in strong nitric acid. When any phosphate is mixed with tin, in filings, or finely granulated, and then covered with moderately strong—50 per cent.—nitric acid, a violent action takes place between the Sn and the acid, resulting in the formation of a

* If any phosphates of the alkaline earthy bases be left, Fe_2Cl_6 should produce a yellowish-white precipitate when added to a portion of the acetic acid solution; if not, no ferric salt need be added to the main portion of the filtrate. (The presence of iron, other than phosphate, is generally indicated by the reddish or ferric acetate colour of the filtrate.) In this case Al and Cr, as well as the metals of the alkaline earths, will still have to be looked for in the filtrate.

stannic hydrate—so-called meta-stannic acid. The phosphates are at the same time dissolved by the nitric. This stannic hydrate (or acid) combines with the P_2O_5 of the phosphates forming a compound quite insoluble in strong or dilute nitric, but decomposed by HCl.

The process is best carried out by evaporating the filtrate, after passing SH_2, in which phosphates have been found, to dryness or nearly so, adding a few grams of tin filings, and covering with moderately strong HNO_3, stirring well and allowing to evaporate on a sand-bath or wire gauze over a flame nearly to dryness. After cooling add dilute HNO_3, warm gently and filter. All the bases will be found in solution as nitrates, and the P_2O_5 will be retained in the white tin oxide residue. Chlorides should be absent.

Before proceeding the nitric acid filtrate must be tested for P_2O_5 by ammonium molybdate.

Although the metals of Group III. arrange themselves very well for analytical purposes *as* a group, there is much difference between some of them in other respects. Fe, Ni, Co, Zn are easily reduced from their oxides, Fe_2O_3, NiO, CoO, ZnO by carbon or CO. MnO is not so easily reduced, and Al_2O_3 and Cr_2O_3 are practically not reduced by C or CO alone at any temperature. The easiest method of reduction in these cases is from their chlorides by sodium or magnesium. By the simultaneous action of Cl and C on the oxides, as:

$$Al_2O_3 + 3C + 3Cl_2 = Al_2Cl_6 + 3CO,$$

the dry chlorides are produced, and may be decomposed by sodium. Cr_2O_3 behaves in exactly the same manner.

The metallic character of chromium, measured by the few salts it forms with acids, is less than that of the other elements in the group. The sulphides also of Cr and Al are not formable by wet processes, whilst all the other metals readily form sulphides from aqueous solutions of their salts. Nickel and cobalt might almost be looked upon as enantiomorphous bodies, from the behaviour of some of their salts, oxides, &c.

With the exception of zinc and aluminium, all these elements have high melting points. Their oxides are all very difficultly fusible bodies. The chlorides are all fusible and volatile. $ZnCl_2$, most *easily followed by* $AlCl_3$ *and* $CrCl_3$ *and* $FeCl_3$, $NiCl_2$, $CoCl_2$, *and* $MnCl_2$, melt but do not vaporise easily, excepting in a current of chlorine gas. The $AlCl_3$ and $CrCl_3$ are scarcely, if at all, reduced by hydrogen at a red heat. The others are moderately easily reduced, $MnCl_2$ being the most difficultly reducible.

The carbides of Al, Cr, Fe, and perhaps also of Mn, when decomposed by water, or HCl, give hydrocarbons of the paraffin series as well as acetylene.

Al, Cr and Fe show a strong tendency to form alums, whilst Ni, Co and Zn do not form this class of salt, and Mn, in this respect, seems to fall between the two sets of metal.

CHAPTER V.

REACTIONS OF THE METALS OF GROUP II.

THIS group comprises the metals mercury, lead, bismuth, copper, cadmium, arsenic, antimony, tin (gold and platinum), which are precipitated from acid solutions (HCl) by means of sulphuretted hydrogen.

As an exercise mix together solutions of $Bi(NO_3)_3$, $HgCl_2$, $CuSO_4$, $CdCl_2$, As_2O_3 (dissolved in HCl), $Pb(NO_3)_2$, $SbCl_3$, $SnCl_2$, and $SnCl_4$, and pass a current of SH_2, without first filtering off the white precipitate which is produced. Filter; pass the gas again through the clear filtrate, to make sure that the metals have been entirely precipitated. Wash the precipitate with hot water; remove a portion from the filter; boil with a little yellow ammonium sulphide, and filter off. A black residue is left, consisting of HgS, PbS, Bi_2S_3, CuS, CdS. The solution contains As_2S_3, Sb_2S_3, SnS and SnS_2 dissolved in the ammonium sulphide.* This can be shown by acidulating with dilute hydrochloric acid when a yellowish precipitate comes down,† consisting of the sulphides of As, Sb, Sn.

This shows that Group II. may be divided, by means of ammonium sulphide or other alkaline sulphide, into two portions.

The name sulphide, in its widest sense, is given to all compounds into which sulphur enters as the electro-negative element. A striking analogy is observable between oxides and sulphides. There is a certain class of sulphides which resembles metallic oxides or bases; another class which plays the part of oxy-acids.‡ Sulphides are therefore divided into sulpho-bases and sulpho-acids. To the latter belong the sulphides of H, As, Sn, Sb (Pt, Au); to the former the sulphides of many metals, especially such of the metals as constitute powerful bases (K, Na, NH_4, Ba, Ca, &c). An electro-positive element, which forms with oxygen an oxide, combines generally also with the same number of sulphur atoms, to form a corresponding sulphide, in which the sulphur is performing similar functions to oxygen.

The resemblance in the constitution of these oxygen and sulphur

* Potassium or sodium-hydrosulphides are nearly as efficient as the ammonium sulphide. It is noticed here, and later, that K and Na sulphides exert a slightly different solvent action on the sulphides of the group to that exerted by ammonium sulphide. There is no doubt that the solubility of these sulphides is due to the formation of a definite double-sulpho salt.

† Yellow ammonium sulphide converts SnS into SnS_2.

‡ Peroxides have their analogues in persulphides. Both can act as acids or electro-negative groups to others with less oxygen or sulphur.

compounds is further borne out by the analogy in their solubility and alkaline reaction :

	Oxy-bases.		*Sulpho-bases.*
OK_2	Potassium oxide, alkaline and soluble.	SK_2	Potassium sulphide, alkaline and soluble.
$O(NH_4)_2$	Ammonium oxide ,,	$S(NH_4)_2$	Ammonium ,, ,,
ONa_2	Sodium ,, ,,	SNa_2	Sodium ,, ,,
BaO	Barium ,, ,,	BaS	Barium ,, ,,
CaO	Calcium ,, ,,	CaS	Calcium ,, ,,
FeO	Ferrous oxide, no reaction, insoluble.	FeS	Ferrous ,, no reaction, insoluble.
ZnO	Zinc ,, ,,	ZnS	Zinc ,, ,,

	Oxy-anhydrides.		*Sulpho-anhydrides.*
As_2O_3	Arsenious anhydride.	As_2S_3	Arsenious sulphide, or sulpharsenious anhydride.
As_2O_5	Arsenic ,,	As_2O_5	Arsenic sulphide, or sulpharsenic anhydride.
Sb_2O_3	Antimonious ,,	Sb_2S_3	Antimonious sulphide, or sulphantimonious anhydride.
Sb_2O_5	Antimonic ,,	Sb_2S_5	Antimonic sulphide, or sulphantimonic anhydride.
SnO_2	Stannic ,,	SnS_2	Stannic sulphide, or sulphostannic anhydride.

	Oxy-acids.		*Sulpho-acids.*
H_3AsO_3	Arsenious acid.	H_3AsS_3	Sulpharsenious acid.
H_3AsO_4	Arsenic acid.	H_3AsS_4	Sulpharsenic acid.
H_3SbO_3	Antimonious acid.	H_3SbS_3	Sulphantimonious acid.
H_3SbO_4	Antimonic acid.	H_3SbS_4	Sulphantimonic acid.
$HSbO_3$	Metantimonic acid.	$HSbS_3$	Sulphometantimonic acid.
H_2SnO_3	Stannic acid.	H_2SnS_3	Sulphostannic acid.

To this list might be added CO_2 and CS_2, which form carbonates and sulphocarbonates respectively, and some others. The analogy here is most complete.

Sulpho-salts are obtained by the mutual action of a sulpho-acid and a sulpho-base upon each other.

Sulphides soluble in water, comprising the sulphides of the alkalies and alkaline earthy metals, are divided into normal sulphides, such as SK_2, $S(NH_4)_2$, SNa_2, BaS ; into sulphydrates (acid sulphides), such as SKH, SNH_4H, BaH_2S_2 ; and *polysulphides*, such as S_2H_2, S_5K_2, $S_5(NH_4)_2$.* The aqueous solutions of the normal and acid sulphides are colourless, and give off SH_2 when treated with dilute hydrochloric acid, without separation of sulphur. Solutions of the polysulphides are yellow, or yellowish-brown, and when treated with hydro-

* The composition of the so-called polysulphides has not been made out with certainty. Indeed, no scientific examination has as yet been made of them. Melted sulphides seem to dissolve a large amount of sulphur, which may be retained in solid solution, or they are very likely the analogues of sulphites and sulphates in which sulphur is acting the part played by oxygen in true sulphites and sulphates, thus: K_2SO_4 : K_2SS_4, and $Na_2S_2O_7$: $Na_2S_2S_7$, &c.

chloric acid give off sulphuretted hydrogen, with separation of white (or precipitated) sulphur.* The number of sulpho-salts known is small compared with the salts of oxy-acids, and they are far less stable than ordinary oxy-salts. The number of sulpho-acids is principally restricted to the acids enumerated above, and these again combine mostly only with the soluble sulphides possessed of an alkaline reaction; or, if combined with the sulphides of the heavy metals, as in certain cases, they are somewhat easily decomposed by chemical agencies. Some are certainly found as minerals.

The following is a list of some sulpho-salts compared with the corresponding oxy-salts;

	Oxy-salts.		*Sulpho-salts.*
Na_2SnO_2	Disodium stannite.	Na_2SnS_2	Sodium sulphostannite.
Na_2SnO_3	Disodium stannate.	Na_2SnS_3	Sodium sulphostannate.
K_3AsO_3	Tripotassium arsenite.	Ka_3AsS_3	Potassium sulpharsenite.
Na_3AsO_4	Trisodium arsenate.	Na_3AsS_4	Sodium sulpharsenate.
$KSbO_2$	Potassium metantimonite.	$KSbO_2$	Potassium metasulphantimonite.
$KSbO_3$	Potassium metantimonate.	$KSbO_3$	Potassium metasulphantimonate.

Treat another portion of the above SH_2 precipitate with NaHO or KHO and filter off. A black residue is likewise left, and on adding dilute HCl to the filtrate, As_2S_3, Sb_2S_3, SnS, and SnS_2 are reprecipitated.

This shows that the *hydrates* of the alkali metals dissolve a portion of the sulphides precipitated by SH_2. The following equations explain the action of the alkaline hydrates:

$$Sb_2S_3 + 6KHO = K_3SbS_3 + K_3SbO_3 + 3OH_2.$$
$$As_2S_3 + 4KHO = HK_2AsS_3 + HK_2AsO_3 + OH_2.$$
$$2SnS + 4KHO = K_2SnS_2 + K_2SnO_2 + 2OH_2.$$
$$2SnS_2 + 4NaHO = Na_2SnS_3 + Na_2SnO_3 + OH_2 + SH_2.\dagger$$

These may be called mixed reactions.

Addition of hydrochloric acid reprecipitates the sulphides, thus:

$$K_3SbS_3 + K_3SbO_3 + 6HCl = Sb_2S_3 + 6KCl + 3OH_2.$$

Hence the metals which are precipitated by SH_2 in Group II. can be subdivided by means of ammonium sulphide or sodium or potassium hydrates into—

A. **Metals whose sulphides act as sulpho-bases**—viz., the sulphides of Hg, Pb, Bi, Cu, and Cd. These are insoluble in ammonium sulphide (HgS dissolves to some extent in potassium

* In some cases hydrogen persulphide, H_2S_2, the analogue of H_2O_2, is formed.

† No SH_2 is given off in this reaction. As excess of NaHO is always used, it may be represented:

$$2SnS_2 + 5NaHO = Na_2SnS_3 + Na_2SnO_3 + 2OH_2 + NaHS.$$

or sodium sulphide; CuS is somewhat soluble in ammonium sulphide).

B. Metals whose sulphides act as sulpho-acids—viz., the sulphides of As, Sb, Sn (Au, Pt).

GROUP II. SUBDIVISION A.

1. **MERCURY,** Hg″.—Occurs native, but is chiefly obtained from cinnabar or mercuric sulphide, HgS, by heating with lime or iron turnings in a distilling apparatus or retort. The element is liquid at ordinary temperatures and down to about − 40° C., at which temperature it crystallises. Both the solid and liquid states exhibit a metalline lustre and colour like silver. It is somewhat malleable whilst solid. It has an atomic weight of 199·71, generally taken as 200. Specific gravity = 13·55 in the liquid and 14·19 in the solid state. The solid melts at − 38·50 C. and boils at 357·25° C. under a pressure of 760 mm. It does not tarnish appreciably in the air, but is very slowly oxidised when gently heated to about 300° C., in an atmosphere of oxygen. Ozone acts more rapidly and at low temperatures. Nitric acid acts readily upon it, even when cold. Sulphuric only when heated and strong. Hydrochloric acid or alkalies have no action. It combines energetically with chlorine, bromine, iodine, and sulphur, also with sodium and potassium and most other metals, excepting iron and platinum, forming amalgams.

EXPERIMENTS.

I. Mercury heated in the open tube boils, evaporates, and condenses again in very *small globules on the cool part, forming a mirror. After heating* for some hours in air the surface lustre becomes less, but no appreciable oxidation takes place in the short time of an experiment.

II. Heated with sulphur, a black solid is formed which sublimes black. On rubbing with a hard substance it becomes somewhat reddish. It is HgS.

III. HCl has no action.

H_2SO_4, when boiling and strong, dissolves it, forming sulphate and liberating SO_2. $Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$. Crystals are obtained on cooling the acid solution.

Nitric acts most readily. Oxides of N are evolved and the nitrate, $HgNO_3$, crystallises out as the liquid cools. On heating this nitrate oxides of nitrogen are given off and HgO left, which also decomposes into Hg and O.

Ammonia and alkalies have no action on the metal.

IV. Iodine combines very readily. The HgI_2 formed sublimes yellow, generally, and becomes pink on rubbing.

DRY REACTIONS.

Add a little finely divided lead or zinc to a few globules of mercury on a watch-glass. The liquid metal mercury becomes thick and pasty by the combination with the solid metal lead or zinc. It is said to form an amalgam. The metallic surfaces must be quite clean or amalgams cannot form. Mixtures of metals, other than mercury, are called alloys. This property of mercury has received an important application in the extraction of gold and silver from poor ores by the so-called amalgamation process, in which the mercury

can be separated again by distillation, the gold or silver being left behind.

When cinnabar, HgS, is roasted in the air, the sulphur is oxidised to SO_2 and metallic mercury sublimes.

Hydrogen and carbon, copper, tin, zinc, &c., reduce HgS at a high temperature, forming with the sulphur SH_2, CS_2 (carbon disulphide), CuS, &c. The native HgS is, however, best reduced by the action of strong bases, such as lime or soda.

Mix a little cinnabar with dry sodium carbonate, and heat in a little tube, sealed up at one end, or blown into a small bulb. Metallic mercury sublimes and forms a mirror in the cold part of the tube; the sulphur is retained by the alkali metal.

Mercury salts, when heated by themselves, out of contact with the air, volatilise or sublime, either without decomposition, such as $HgBr_2$, $HgCl_2$, Hg_2Cl_2, HgI_2, HgS, HgICN; or they are decomposed into oxide or metal as HgN_2O_6, the nitrate, which gives $HgO + N_2O_4 + O$. Salts of mercury with fixed acids as the phosphate or chromate, leave fixed residues of acid or oxide (Cr_2O_3).

Sulphates of mercury decompose on heating into SO_2, HgO and O, and finally metallic Hg. Carbonate into HgO and CO_2 and finally metal.

Probably the most delicate test for mercury is a piece of metallic gold, a coin, which becomes whitened by an exceedingly small amount of Hg. Bright metallic copper comes next in delicacy in showing this test.

An amalgam of 4 parts of tin and 1 part of mercury is employed in the manufacture of looking-glasses.

REACTIONS IN SOLUTION.

Mercury forms two series of salts: mercurous and mercuric.

In mercurous salts the element exhibits less extent of energy of combination than in mercuric salts. As, for instance, mercurous oxide, Hg_2O, calomel, Hg_2Cl_2; and mercuric oxide, HgO, corrosive sublimate, $HgCl_2$. In the former case it is supposed that the metal is in some way combined with itself as Hg—Hg or Hg—Hg, whilst

```
Hg—Hg      Hg—Hg
  \ /       |   |
   O       Cl   Cl
```

in the latter the whole extent of the energy of the mercury-atom is expended on the substance with which it is combined.

Mercury readily dissolves even in cold nitric acid, forming mercurous nitrate, if the mercury is in excess, and mercuric nitrate, if the acid is in excess and hot. These salts have the composition—or can be represented as:

$Hg_2(NO_3)_2$	and	$Hg(NO_3)_2$
Mercurous nitrate		Mercuric nitrate.

Mercurous oxide exhibits a tendency to combine with another

atom of oxygen, or, when exposed to heat, to part with one atom of mercury, and the remainder to become converted into mercuric oxide. Hence mercurous salts act as reducing agents.

As mercurous chloride is insoluble, the reactions of mercurous salts will be considered in connection with the reactions of silver and lead in Group I.

In order to study the reactions of mercuric salts, a solution of *mercuric nitrate*, $Hg(NO_3)_2$, or *mercuric chloride*, $HgCl_2$ (corrosive sublimate), may be employed. Not many mercury salts are *very* soluble and few are really insoluble in water.

SH_2 (group-reagent) added to $HgCl_2$ gives a black precipitate of mercuric sulphide, HgS. The precipitation is marked by characteristic changes of colour. Accordingly as sulphuretted hydrogen water is added in small quantities, or the gas passed slowly through the solution, it produces at first a perfectly white precipitate, and on the addition of more SH_2, a yellow precipitate which passes through dirty yellow to brown, and becomes black only when excess of SH_2 has been added to the mercuric salt. The white, yellow, or brown precipitate is a varying mixture of HgS and $HgCl_2$. HgS is insoluble in nitric or hydrochloric acid and in yellow ammonium sulphide, potassium hydrate, or potassium cyanide, soluble, however, in aqua regia and in potassium or sodium sulphide in the presence of sodium hydrate, but insoluble in their sulphydrates. Long digestion with concentrated nitric acid converts the black HgS into a white body, probably a compound of $2HgS + Hg_2(NO_3)_2$ (?). It may only be a mixture however.

Ammonium sulphide gives the same precipitate.

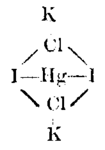
NaHO or KHO added in excess produces a yellow precipitate of mercuric hydrate, $Hg(HO)_2$ insoluble in excess.

NH_4OH produces a white precipitate, from the chloride, of mercuric ammonium chloride, $NH_2Hg''Cl$, known as "white precipitate."

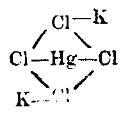
Sodium or potassium carbonates give a reddish-brown basic precipitate.

KI gives a bright red precipitate of mercuric iodide, HgI_2, soluble either in excess of potassium iodide or of the mercuric salt.*

* $HgI_2 2KI$. This is also known as a double salt, and is probably—



but no experimental evidence of this formula is to hand to date. The chloride $HgCl_2$ also forms a crystalline compound with 2KCl, which may be similarly expressed :



KCy gives with mercuric nitrate (not the chloride) a white precipitate consisting of cyanide and nitrate, soluble in excess, not decomposed by boiling with alkalies or alkaline carbonates, but only by SH_2.

Mercuric salts are readily reduced to mercurous salts:

$SnCl_2$ (stannous chloride) gives with mercuric salts a white precipitate of mercurous chloride, Hg_2Cl_2, which, when boiled with excess of the reagent, is reduced to grey metallic mercury. On pouring off the solution and boiling the grey precipitate with HCl, the mercury is obtained in little globules.

$FeSO_4$ (ferrous sulphate) reduces $Hg(NO_3)_2$, but not $HgCl_2$, to the metallic state.

Cu, Zn, Pb, Sn, Cd, and Fe precipitate metallic mercury from mercuric solutions, provided they are not too acid. They do not all act at the same rate.

If a strip of bright metallic copper be employed, a silvery-white deposit of metallic Hg is obtained, which, when gently rubbed, shows a bright metallic lustre, and gives, after drying and heating in a dry and narrow test-tube, or bulb-tube (see Fig. 9, p. 91), a sublimate of metallic mercury.

Mercuric salts are first reduced to mercurous salts, and finally to metallic mercury.

2. **LEAD.**—Only a slight precipitate of PbS is for the most part obtained in Group II., since the greater part of the lead is removed in Group I. as $PbCl_2$. It happens frequently that this small quantity of lead is not precipitated by SH_2, on account of the solution being too acid (HCl), or too concentrated, in which case a little lead is found in Group III., and is often mistaken for some other metal. It is necessary, therefore, to dilute a portion of the filtrate from Group II. considerably, and to pass a current of SH_2 through, in order to make sure of the presence of lead, especially so when lead has been discovered in Group I.; and, if a precipitate be obtained, to pass the gas once more through the whole of the filtrate, after having diluted it considerably or even neutralised to some extent by adding ammonia.

3. **BISMUTH,** Bi''' and ^{v}.—This metal is principally found native; also in combination with oxygen and sulphur, as bismuth ochre, Bi_2O_3, from the decomposition of bismuth glance, Bi_2S_3, and in the form of sulpho-salts, as kobellite, Bi_2S_3, 3PbS, and needle ore, Bi_2S_3, 2PbS, Cu_2S.

The metal is highly crystalline, brittle, of a white colour, with a red tinge. Atomic weight, 257·52; specific gravity, 9·80; melts, 266°·8, and boils between 1090° and 1450°.

It is not malleable at all but powders up easily in a mortar.

Water and air have little or no effect at ordinary temperatures. It expands on solidifying from fusion similarly to ice. The metal is seldom employed in a pure state, but is much used for alloys where fusibility is desired.

EXPERIMENTS.

I. Heated in tube in air. Rapid oxidation takes place, fine coloured films pass over surface of melted metal and a yellow or yellowish-red oxide forms. The oxide is very fusible and darkens on heating.

II. Heated with sulphur combination takes place very readily to Bi_2S_3, a nearly black, crystalline but non-volatile substance; it melts readily.

III. Hydrochloric scarcely acts at any temperature. Sulphuric acts very slowly and only when concentrated.

Nitric dissolves it most readily with evolution of fumes of oxides of nitrogen, and formation of $Bi3NO_3$ which crystallises readily when slightly evaporated in dish. *Ammonia and soda have no action either on metal or oxide.*

The oxide dissolves readily in acids and the solutions give crystals on evaporation. All the salts are colourless unless the acid be coloured.

DRY REACTIONS.

Salts of bismuth are reduced with ease on charcoal by the blowpipe, covering the charcoal with an incrustation of oxide, orange-yellow, while hot, lemon-yellow, when cold, passing at the edges into a bluish-white. The incrustation can be driven from place to place by either flame, without colouring the outer flame. (Distinction from lead.) Heated with borax or microcosmic salt, Bi_2O_3 gives beads which are yellowish, when hot, and colourless, when cold. All bismuth compounds can be reduced to the metallic state by heating on charcoal with sodium carbonate in the inner or reducing flame. The metallic bead is brittle. (Distinction from lead and silver beads.)

REACTIONS IN SOLUTION.

Bismuth dissolves readily in nitric acid, forming $Bi(NO_3)_3$. Other acids have little or no effect, and few real bismuth salts are known. (See its position in the "Natural Series.")

SH_2 (group-reagent) gives a brownish-black precipitate of bismuthous sulphide, Bi_2S_3, insoluble in dilute acids, in alkalies, and in alkaline sulphides; soluble in concentrated nitric acid.

Alkaline sulphides give the same precipitate.

KHO, NaHO, and NH_4OH produce a white precipitate of bismuthous hydrate, $Bi(OH)_3$, insoluble in excess.

Alkaline carbonates throw down a white bulky precipitate of basic carbonate $(BiO)_2CO_3$, in which the compound radical bismuthyl, BiO, takes the place of hydrogen. The precipitate is insoluble in excess.

$K_2Cr_2O_7$ gives a yellow precipitate of basic chromate $(BiO)_2Cr_2O_7$, readily soluble in dilute nitric acid, insoluble in potassium hydrate. *(Distinction from lead chromate.)*

H_2SO_4 gives no precipitate. (Distinction from lead.)

KI produces a brown precipitate of bismuthous iodide, BiI_3, soluble in excess to a reddish solution.

KCy produces a white precipitate, insoluble in excess, soluble in acids.

Bismuthous salts are decomposed by water, a basic salt being

precipitated. The addition of an acid redissolves the precipitate. This constitutes the most characteristic reaction for bismuthous salts. The salt most readily precipitated is the chloride ($BiCl_3$). It can be prepared from the nitrate by precipitating the oxide first, and then filtering and dissolving the precipitate off the filter with hot dilute hydrochloric acid. Large excess of acid should be avoided.

OH_2 gives with $BiCl_3$ a white precipitate of bismuthous oxychloride, BiOCl, which is almost absolutely insoluble in water, but soluble in hydrochloric acid, from which it is reprecipitated on the addition of ammonium or sodium chloride. BiOCl is insoluble in tartaric acid. (Distinction from antimony.)

Metallic zinc precipitates bismuth from its salts.

Bismuthous salts exhibit a strong tendency to form basic salts, showing that Bi is only a feebly positive element.

Other oxides of bismuth in addition to Bi_2O_3 are known, *e.g.*, bismuthic oxide or anhydride, Bi_2O_5 and Bi_4O_7 and BiO no doubt also exist.

4. **COPPER,** Cu''.—This metal is found native; also in combination with oxygen and sulphur, as red copper ore or ruby ore, Cu_2O, as vitreous copper or copper glance, Cu_2S, and indigo copper or blue copper, CuS; more frequently as copper pyrites, Fe_2S_3,Cu_2S, and variegated copper or horseflesh ore, $Fe_2S_3,3Cu_2S$, also as fahl ore, bournonite, &c.; in combination with carbonic acid, as basic carbonate, malachite, $CuCO_3.Cu(OH)_2$, and azurite, mountain blue, or copper azure, $2CuCO_3,Cu(OH)_2$; with sulphuric acid as blue vitriol, $CuSO_4 5OH_2$, with phosphoric acid, as phosphorocalcite, libethenite; with arsenious acid, as tennantite; with silicic acid, as dioptase, and others.

Copper is extracted from its sulphides by a combination of oxidising and reducing processes. It is the only metal of a decided red colour. Its atomic weight = 63·17; specific gravity 8·92, and melts at 1054° C.

It is very tough and malleable, takes a fine polish, and is one of the best conductors of heat and electricity. Copper forms many alloys of great practical importance as different kinds of brass with zinc, and bronzes with tin and other metals. It enters also into the composition of many colours.

On exposure to air, it oxidises very slowly at ordinary temperatures, but rapidly when heated to redness. Water has no action on copper at any temperature, but most acids attack it especially if exposed to air at the same time. Alkalies, including lime and especially ammonia, also act upon it under similar circumstances.

EXPERIMENTS.

1. Heated in air a clean metallic surface changes through many colours, finally becoming black; a black crust detaches, this is CuO; it does not melt or change on further heating.

N.B.—A wire melts easily in the Bunsen flame, but it is difficult to melt the metal in an ordinary glass-tube.

II. With sulphur in tube it combines readily, forming a bluish-black mass which melts easily and is crystalline. It is CuS or partly Cu_2S, depending on temperature.

III. Hydrochloric acid does not act appreciably on copper, either cold or hot, when the metal has a clean surface.

Strong sulphuric dissolves the metal when boiled on it, SO_2 gas escaping. $CuSO_4$ is formed. $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$.

Nitric dissolves it rapidly, oxides of nitrogen being at the same time formed. The greenish-blue liquid on evaporation gives crystals of copper nitrate $Cu2(NO_3)$, which are very soluble in water.

Organic acids act only in presence of air or on oxidised surfaces.

The oxide as formed in (I.) dissolves quickly in the acids and gives a green solution with HCl, a blue with H_2SO_4, and a blue-green with HNO_3. It also dissolves in ammonia, forming a deep blue solution.

Soda, NaHO, does not dissolve it.

IV. Metallic copper is acted upon by ammonia, in contact with air at same time; the same blue compound as from the oxide is formed. The alkalies and also lime, CaH_2O_2, act on the metal in presence of air, a green basic carbonate being formed.

Solutions of chlorides or nitrates in presence of air, also corrode the metal somewhat rapidly.

Organic acids, as acetic, CH_3CO_2H, also act somewhat rapidly on copper when air has access. A greenish coating forms.

Unless the copper surface be absolutely clean, an action is observable in a few minutes on warming with many organic compounds even when air and water are absent.

DRY REACTIONS.

Copper minerals are very numerous; and as many of them exhibit precisely similar blowpipe reactions, a knowledge of their physical character is indispensable to enable the student to distinguish readily between them. Wet tests are, perhaps, most delicate for copper.

The most characteristic dry reaction is that which copper compounds give, when heated in a bead of borax or microcosmic salt before the blowpipe flame. The bead is green whilst hot, blue on cooling. Most copper compounds, when heated on platinum wire in the inner flame, impart an intense green colour to the outer flame. All copper compounds are reduced when heated in the inner flame on charcoal, together with sodium carbonate and potassium cyanide, yielding red metallic scales or globules. Sulphides give off SO_2, when roasted in an open tube, and leave CuO behind. Malachite or azurite gives off water and carbonic anhydride when gently heated in a tube. Blue vitriol loses water, sulphurous anhydride and oxygen, and leaves cupric oxide. Cupric phosphate, arsenate, and silicate fuse to coloured glasses.

EXAMINATION IN SOLUTION.

Hydrochloric acid in the presence of air dissolves copper slightly, forming Cu_2Cl_2; nitric acid is the most active solvent for copper, forming cupric nitrate. Sulphuric acid (concentrated) dissolves copper, on heating.

The sulphate, nitrate, and chloride are soluble in water.

Cuprous salts are mostly insoluble.

SH_2 (group-reagent) gives a brownish-black precipitate of hydrated cupric sulphide, CuS, insoluble in dilute acids; slightly soluble in yellow ammonium sulphide; soluble with decomposition in nitric acid; completely soluble in potassium cyanide; insoluble in potassium and sodium sulphides or caustic alkalies. CuS is rapidly oxidised to $CuSO_4$ by exposure to the air; it is insoluble in hot dilute sulphuric acid.

$(NH_4)_2S$ produces the same precipitate, somewhat soluble in excess, especially in yellow ammonium sulphide.

NaHO or KHO gives a light-blue precipitate of cupric hydrate, $Cu(HO)_2$. The precipitate turns black on boiling and becomes denser, losing some water of hydration. Three molecules of $Cu(HO)_2$ lose two molecules of OH_2 and leave $3CuO,OH_2$. In the presence of many organic substances such as grape sugar, tartaric, and a number of organic acids, especially di- and tri-basic acids and substances of the nature of urea, N_2H_4CO, the precipitate dissolves to a deep blue solution, whence the whole of the copper is reprecipitated on boiling in the form of bright red cuprous oxide, Cu_2O.

Na_2CO_3 or K_2CO_3 produces a greenish-blue basic carbonate, of the composition $CuCO_3,Cu(OH)_2$, carbonic anhydride being evolved. This precipitate is converted on boiling into the black precipitate of $3CuO,OH_2$. It is soluble in ammonium hydrate to an azure-blue, and in potassium cyanide to a colourless fluid containing a soluble double cyanide, $Cu(CN)_2 2KCN$.*

Ammonium hydrate or its carbonates, when added in small quantities, produces a greenish-blue precipitate of a basic salt, which dissolves readily in excess of the reagents, and forms a magnificent azure-blue liquid—a blue which is perceptible if a solution contains only small traces of copper. The blue solution contains ammonio-cupric sulphate, $SO_4\left(\begin{matrix}NH_3.NH_3\\NH_3.NH_3\end{matrix}\right)Cu,OH_2$,† whence the black cupric oxide separates on boiling with sodium hydrate and NH_3 escapes.

This tendency of ammonia to combine with cupric hydrate induces

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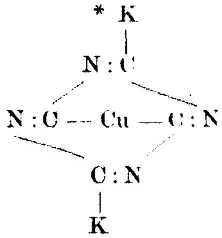


† The basis of this compound and perhaps all ammonio-compounds may be a substituted ammonia, $\begin{matrix}NH_2\\NH_2\end{matrix}Cu + H_2O$, or a cupramine, hydrated when in combination or solution.

metallic copper to combine with oxygen even at the ordinary temperature when in contact with ammonia, forming a compound which is utilised in certain technical processes in connection with paper and celluloses.

KCy gives a greenish-yellow precipitate of cupric cyanide, $CuCy_2$, soluble in excess. SH_2 produces no precipitate from this solution.

K_4FeCy_6 gives a reddish-brown precipitate of cupric ferrocyanide, Cu_2FeCy_6, insoluble in dilute acids, decomposed by potassium or sodium hydrate, with separation of $3CuO,OH_2$. Even in very dilute solutions of copper salts a brownish colour is produced—best seen by looking through a long layer of the solution. K_4FeCy_6 is another most delicate reaction for copper salts.

Metallic zinc, or iron, precipitates metallic copper, especially in the presence of a little free hydrochloric acid. If a few drops of a slightly acidulated dilute copper solution are placed on platinum foil (the lid of a platinum crucible), together with a small piece of sheet zinc, the platinum becomes rapidly coated with a reddish film of metallic copper, visible even in the case of very dilute solutions, an equivalent quantity of zinc being dissolved.

Copper resembles mercury in existing in combination in two forms; or exhibiting two degrees of extent of combination energy with other elements expressed by the terms cuprous and cupric. For instance, it combines with oxygen to form an oxide, CuO, and one of half the oxygen content, Cu_2O, and similarly with sulphur, CuS and Cu_2S, and with the halogens ($CuCl_2$ and Cu_2Cl_2), &c.

Some of the chemical energy of the copper atom is doubtless expended on itself or latent in cuprous compounds, *e.g.*, $Cu_2O =$

Cu—Cu
\O/ They are generally less stable under physical or chemical changes than cupric compounds.

Cuprous oxide when treated with concentrated hydrochloric acid forms cuprous chloride, Cu_2Cl_2, which is colourless when pure. Other acids decompose it into metallic copper and cupric oxide, which latter dissolves in the acid as a cupric salt. Cuprous chloride, when moist or in solution, attracts oxygen very rapidly, and is a powerful reducing agent. It combines with CO, and is used in gas analysis for this reason. It is also a good reagent for some unsaturated low carbons as C_2H_2, acetylene and C_2H_4, ethylene, and others.

Cuprous Compounds.—To a solution of cuprous chloride, Cu_2Cl_2, in concentrated hydrochloric acid, add

OH_2, a white precipitate of Cu_2Cl_2 is produced, because the diluted acid is not able to dissolve the salt.*

KHO gives a yellow precipitate of cuprous hydrate, $Cu_2(HO)_2$, insoluble in excess; it attracts oxygen very rapidly, being converted into cupric hydrate.

KI, in the presence of sulphurous acid or ferrous sulphate, precipitates from cupric salts greenish-white cuprous iodide, Cu_2I_2,

* This solution in HCl is undoubtedly a compound, $Cu_2Cl_2 2HCl$.

soluble in excess of the iodide.* Both sulphurous acid and ferrous sulphate are reducing agents, which, by the absorption of oxygen from the cupric salts, are converted into H_2SO_4 and $Fe_2(SO_4)_3$, thus:

$$(1)\quad \underset{\text{Cupric sulphate}}{2CuSO_4} + 2FeSO_4 = \underset{\text{Cuprous sulphate}}{Cu_2SO_4} + Fe_2(SO_4)_3.$$

$$(2)\quad Cu_2SO_4 + 2KI = \underset{\text{Cuprous iodide}}{Cu_2I_2} + K_2SO_4.$$

NH_4SCy and a reducing agent, as H_2SO_3, forms white cuprous sulphocyanate, $Cu_2(SCy)_2$, insoluble in water, and not affected by dilute acids excepting nitric. In the presence of H_2SO_3 this precipitate is very insoluble, and gives a good method of separation of copper from many other metals.

5. **CADMIUM**, Cd″. Cadmium occurs in nature along with zinc minerals and resembles that metal to some extent both in chemical and physical properties. It is not quite so crystalline as zinc, nor has it such a blue colour.

Its atomic weight is 111·84. Specific gravity 8·60. It melts at about 315° C., and boils at about 770° C. It can therefore be distilled like mercury or zinc, and indeed is generally obtained from the first portions of zinc distillate in the extraction of that metal. It burns with a brown flame when heated in air or oxygen, but does not act very rapidly on water. Acids, especially nitric, dissolve the metal rapidly. Being less crystalline than zinc, it may be rolled or hammered at the ordinary temperature. Zinc requires heating for this purpose. Alkalies also dissolve it with evolution of hydrogen.

Greenockite, CdS, is the only well-known cadmium mineral, but most zinc ores contain small quantities. It is employed in some alloys to induce fusibility.

EXPERIMENTS.

I. Heated in tube shows colours finally passing into brown ash or oxide, CdO, which does not melt or volatilise, but generally a little metal will volatilise and form a dark brown sublimate or mirror in the tube. The oxide formed on the surface on gently heating, below melting, adheres very closely.

II. Sulphur does not unite *very* easily with cadmium when heated in the tube, but more easily than with zinc.

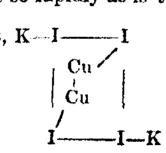
On heating to the vapourising point combination takes place very energetically, a beautiful yellow sulphide, CdS, being formed; this body is rosy red when hot.

III. Dilute warm hydrochloric, sulphuric, and nitric acids dissolve the metal and form colourless crystalline compounds which are not deliquescent. The acids when cold and dilute act but slowly.

The oxide dissolves readily in the three acids. Ammonia also dissolves the oxide, but not very rapidly after it has been heated strongly.

IV. Alkalies also dissolve the metal, but not so rapidly as is the case with zinc.

* This is another double salt,



DRY REACTIONS.

Cadmium compounds when mixed with sodium carbonate and heated on charcoal in the inner blowpipe flame, give a characteristic brown incrustation—*i.e.*, they are readily reduced to the metallic state; but the metal being highly volatile, is reoxidised on its passage through the outer flame. Cadmium is recognised with more difficulty when it is in combination with zinc, as for instance in cadmiferous blende. By heating, however, a mixture of blende and sodium carbonate and potassium cyanide for a few moments only on charcoal a slight brown incrustation is generally obtainable, before the zinc is volatilised. Cadmium oxide turns the bead of borax or microcosmic salt yellowish whilst hot, colourless when cold, but this is no use as a test when other substances are present.

REACTIONS IN SOLUTION.

Most ordinarily occurring cadmium compounds as sulphate, chloride, iodide, nitrate, acetate, &c., are soluble in water, and all others are soluble in acids. They are mostly colourless.

SH_2 (group-reagent) gives from dilute solutions a fine yellow precipitate of cadmium sulphide, CdS, used as a permanent yellow paint, insoluble in alkaline sulphides, caustic alkalies, or potassium cyanide; insoluble in cold, but soluble in hot, dilute nitric and hydrochloric acids; soluble also in dilute sulphuric acid. (Distinction from copper.)

Hence the separation of cadmium by means of SH_2, especially from acid solutions, is frequently left either incomplete, or is not effected at all, in Group II., unless the precaution be taken of nearly neutralising the free acid with ammonia, before passing SH_2, as well as neutralising the mineral acid as fast as it is liberated by the SH_2.

$(NH_4)_2S$, same precipitate.

KHO, a white precipitate of cadmium hydrate, $Cd(HO)_2$, insoluble in excess.

NH_4OH, same precipitate, soluble in excess.

Pure carbonate free from caustic alkali gives a white precipitate of cadmium carbonate, $CdCO_3$, insoluble in excess.

KCy gives a white precipitate of cadmium cyanide, $CdCy_2$,* soluble in excess. Sulphuretted hydrogen precipitates CdS from this solution. (Distinction from copper.)

Metallic zinc precipitates cadmium from its solutions as a crystalline powder, which assumes metallic lustre on rubbing with a hard substance.

Separation of the metals of Subdivision A, Group II.—viz., mercury, lead, bismuth, copper, cadmium, whose sulphides are insoluble in ammonium sulphide or sodium hydrate.

The precipitate produced by the group-reagent SH_2, which is insoluble in ammonium sulphide or sodium hydrate, may consist of

* See double cyanides.

all the five sulphides, or only of one, two, &c. A precipitate of a bright yellow colour, *e.g.*, would be indicative of cadmium sulphide only. If the precipitate is black, it is necessary to examine for all the five metals.

It has already been seen that the sulphides of the metals of this subdivision are—

1st. Insoluble in alkalies and alkaline sulphides, and

2nd. Insoluble in dilute acids, or nearly so; but soluble in concentrated acids.

Concentrated nitric acid (free from chlorine), diluted with its own bulk of water, dissolves four out of the five sulphides—viz., PbS, Bi_2S_3, CuS, and CdS, with separation of sulphur;* mercuric sulphide being completely soluble only in aqua regia. Hence by boiling with dilute nitric acid (in the absence of HCl) mercury may be separated from the other metals of subdivision A. Concentrated nitric acid converts PbS partially into $PbSO_4$, by the simultaneous oxidation of the sulphur. HgS would be, therefore, found in the residue, as well as $PbSO_4$ and S. But the whole of the PbS can be converted into sulphate only by boiling with fuming nitric acid, and as lead sulphate is slightly soluble in concentrated nitric acid, the lead would not be entirely removed as sulphate. This difficulty is overcome by boiling the whole of the sulphides with dilute nitric acid, as mentioned, then diluting with water and adding dilute sulphuric acid and, lastly, when cold, adding to the solution its own bulk of alcohol (methylated spirit). If a residue is left it may be white, indicative of the presence of $PbSO_4$, or black, from the presence of HgS. Sulphur may also be left. The solution contains the metals Bi, Cu, Cd.

Examination of the Residue.—Lead sulphate dissolves readily in certain salts, such as ammonium acetate or tartrate, also in strong HCl when hot. By treating the residue, therefore, with a concentrated solution of ammonium acetate, the $PbSO_4$ is dissolved out. The absence of mercury compounds may be inferred, if no black, but only a yellow, residue of sulphur is left, and if no mercury has been indicated by the reactions in the dry way. The presence of both lead and mercury should, however, invariably be confirmed by special tests—viz., the lead by means of potassium chromate, and the mercury by heating the dry residue in a bulb tube with dry sodium carbonate.

Examination of the Solution.—It has been seen that NH_4OH precipitates $Bi(HO)_3$, which is insoluble in excess, whilst $Cu(HO)_2$ and $Cd(HO)_2$ are likewise precipitated, but are soluble in excess. If a white precipitate be obtained on adding NH_4OH, the inference is that bismuth is present. (Should the lead not have been removed entirely, some $Pb(HO)_2$ would be also precipitated.) The precipitate is filtered off and well washed, then redissolved in a little hydrochloric acid, and precipitated by the addition of much water.† The ammoniacal filtrate is of a fine azure-blue colour, when

* A little H_2SO_4 is also formed.

† Much water here means pouring the 3 or 5 cc. of solution into about 500 cc. of water.

copper—even in small quantities—is present. If colourless, and if, by the addition of SH_2 a fine yellow precipitate comes down, the inference is that no copper is present, but only cadmium. If a black precipitate comes down, on passing the gas through the slightly acidulated (HCl) solution, the presence of copper and possibly of cadmium is indicated. These two metals can be separated either by means of KCy (CdS being insoluble in potassium cyanide), or dilute sulphuric acid (CuS being insoluble in hot dilute sulphuric acid). Filter again; in the one case copper is left in solution, in the other cadmium. It is not difficult to identify these two metals by special tests.

The separation of the metals mercury, lead, bismuth, copper and cadmium, is therefore based upon—

1st. The insolubility of HgS in nitric acid.

2nd. The formation of $PbSO_4$, and its solubility in ammonium acetate.

3rd. The insolubility of $Bi(HO)_3$ in excess of ammonium hydrate.

4th. The insolubility of CuS in dilute sulphuric acid, or its solubility in potassium cyanide.

A tabular scheme for their separation is given in the Analytical Tables, Table II.

GROUP II. SUBDIVISION B.

1. **TIN**, Sn″ and ^{iv}.—This metal is found in nature mainly in the form of tinstone or cassiterite, SnO_2, sometimes combined with sulphur, as tin pyrites, SnS_2 (bell-metal ore). The metal is obtained by the reduction of its oxide, SnO_2, by carbon. It is white with a slight yellow tint. Its atomic weight = 117·70; specific gravity, 7·29; melting point, 230·9° C.; boils between 1450° and 1600° C. Soft, but does not mark paper like lead. Tin, although very malleable and ductile, is a very crystalline metal, as may be noticed when a piece of the metal is treated with a dilute acid—crystalline markings appear—or when a piece is bent, when a creaking, due to rupture of contact between crystal faces, is caused.

Tin is much used alone and also to form alloys with Cu or Sb or Pb, also with Hg. Tin "ware" is iron coated with tin: a superficial alloy only.

The metal does not oxidise in air, excepting when heated to its melting point. Water has no action at ordinary temperatures, and dilute acids little, if any. Concentrated HCl dissolves it when heated or when in presence of platinum.* Strong nitric acid converts it into metastannic acid. Alkalies also act on the metal, oxidising it, and then combining with the oxide, forming stannates. It exhibits two, if not three, stages or degrees of energy in its combinations with other substances; for instance, oxides, SnO, Sn_2O_3, SnO_2.

* It may be remarked that it is extremely likely that a perfectly pure metal, even one ordinarily considered positive in chemical character, would be unacted upon by acids, the small amount of impurity in ordinary metals sufficing to set up a voltaic action under the influence of which they are attacked more easily.

EXPERIMENTS.

I. Heated in tube in air; after melting coloured films pass over surface of globule. A grey ash forms which does not melt but becomes yellow-brown when hot, pale yellow when cold. It is SnO_2.

II. With sulphur combination takes place readily with heat evolution. The product is blackish, soft and fusible, crystalline inside = SnS.

III. Hot hydrochloric dissolves tin, hydrogen escapes and tin chloride, $SnCl_2$, is formed. On evaporating in dish white crystals may be obtained. A large quantity of water added to the crystals will produce a white amorphous hydrated compound.

Sulphuric has little or no action unless boiling, and then only slowly.

Nitric acid acts violently, red gases escape and a white powder is formed which does not dissolve either in the acid or in water; strong HCl dissolves it slowly. Oxide of tin prepared as in I. is almost insoluble in all acids. Strong soda, NaHO dissolves it to some extent.

IV. Ammonia is without action on the metal or oxide. KHO and NaHO in concentrated solution act on the metal, hydrogen being slowly evolved. The presence of another metal, as iron or platinum, assists this solution in alkalies by forming a galvanic couple.

DRY REACTIONS.

When tin minerals are fused on charcoal, with sodium carbonate and potassium cyanide, in a strongly reducing flame, they yield small globules of tin which are malleable, and the charcoal becomes covered with a white coating of SnO_2. If this white incrustation be treated with a solution of cobaltous nitrate, and strongly heated, it assumes a bluish-green colour, which is characteristic of tin, but is not to be trusted to when other metallic oxides are present. Insoluble stannic oxide, SnO_2, or the native oxide, may also be fused with caustic potash in a silver crucible, and thus converted into potassium stannate, soluble in water; or it may be rendered soluble by fusion on charcoal with 3 parts of sodium carbonate and 3 of sulphur, when sodium sulphostannate is formed, which is soluble in water, but is decomposed and precipitated as SnS_2 by means of hydrochloric acid.

By introducing into a borax bead—in which sufficient cupric oxide has been diffused to render the bead faintly blue—traces of a stannous compound and heating it in the reducing flame, the bead turns reddish-brown or forms a ruby-red glass, because of the reduction of the copper compound to red cuprous oxide.

Tinstone being insoluble in acids, must be fused with alkaline carbonates and a reducing agent, such as potassium cyanide, charcoal, or black flux (ignited Rochelle salt), when metallic tin is obtained. Tin dissolves slowly in hot hydrochloric acid; readily in aqua regia with formation of $SnCl_4$. Nitric acid converts tin into metastannic acid, $Sn_5O_5(HO)_{10}$, which by evaporation and ignition is converted into SnO_2. Tin forms very few real salts. Its metallic or basic nature is but slight. It is, in fact, a member of the carbon group, and shows a greater tendency to form acid than basic compounds. All the members of this group form an oxide, MO_2, which exhibits acid characters.

One atom of tin is capable of combining either with two or four

atoms of chlorine, &c. In stannous chloride, $SnCl_2$, the metal exists as a dyad, and in stannic chloride, $SnCl_4$, as a tetrad element. It is capable of forming two series of salts, of oxides, sulphides, &c., viz:

Stannous compounds.		*Stannic compounds.*	
$SnCl_2$	Stannous chloride.	$Sn^{iv}Cl_4$	Stannic chloride.
SnO	" oxide.	$Sn^{iv}O_2$	" oxide (anhydride).
$SnSO_4$	" sulphate.	$Sn^{iv}S_2$	" sulphide.
SnS	" sulphide.		

Stannic acid, H_2SnO_3, combines not only with the strong alkali bases, OK_2, ONa_2, but even with stannous oxide, SnO, to form stannates, *e.g.*, K_2SnO_3, dipotassium stannate; $SnSnO_3$, stannous stannate.

REACTIONS IN SOLUTION.

A. *Stannous compounds.*—A solution of stannous chloride, $SnCl_2$, is employed.

SH_2 (group-reagent) gives a dark-brown precipitate of stannous sulphide, SnS, insoluble in ammonia; nearly insoluble in normal ammonium sulphide, but readily dissolved in the presence of sulphur or by the yellow sulphide; from this latter solution it is reprecipitated as yellow stannic sulphide, SnS_2, on the addition of hydrochloric acid. It is also soluble in potassium or sodium hydrate, from which hydrochloric acid precipitates SnS unchanged. Soluble in boiling hydrochloric acid.

$(NH_4)_2S$, gives the same precipitate. Soluble in large excess.

KHO or $NaHO$ gives a white bulky precipitate of stannous hydrate $2SnO,OH_2$, soluble in excess to potassium stannite, K_2SnO_2.

Ammonium hydrate or carbonate, same precipitate, insoluble in excess.

By far the most interesting reactions are based, however, upon the tendency of stannous salts to become converted into stannic salts. $SnCl_2$ combines directly with two more atoms of chlorine to become $SnCl_4$, whereby the chemical affinities of tin for chlorine become satisfied. Stannous compounds may be viewed as unsatisfied bodies, which can deprive certain other bodies of chlorine, oxygen, &c.

$HgCl_2$ added to a solution of $SnCl_2$, produces first a white precipitate of mercurous chloride, Hg_2Cl_2, and when boiled with excess of $SnCl_2$, a greyish powder of metallic mercury.

$CuCl_2$ is reduced by $SnCl_2$ to cuprous chloride, Cu_2Cl_2, with formation of $SnCl_4$.

Fe_2Cl_6 yields two atoms of chlorine to $SnCl_2$, forming $SnCl_4$, and leaving two molecules of $FeCl_2$. The yellowish solution turns green or colourless.

Potassium permanganate or dichromate solutions, in the presence

of an acid, become colourless and green respectively when $SnCl_2$ is added to them.

$AuCl_3$ gives with $SnCl_2$ a purple precipitate (purple of Cassius), which may be viewed as $Au_2 + 3SnO_2$. The change may be expressed thus:

$$2AuCl_3 + 3SnCl_2 + 6OH_2 = Au_2 + 3SnO_2 + 12HCl.$$

This is a most delicate reaction, especially when the $SnCl_2$ contains a little $SnCl_4$.

B. *Stannic compounds.*—A solution of stannic chloride, $SnCl_4$, or bromide $SnBr_4$ is almost the only form in which it can be employed for these tests. These compounds are decomposed by much water, so the solution must be fairly strong and have a slight excess of acid (HCl).

SH_2 (group-reagent) gives a yellow precipitate of stannic sulphide, SnS_2, readily soluble in alkaline sulphides, potassium hydrate, boiling concentrated hydrochloric acid, and aqua regia; soluble, although somewhat difficultly, in ammonium hydrate (distinction from SnS), and insoluble in ammonium hydrogen carbonate.

$(NH_4)_2S$, same precipitate, soluble in excess.

KHO or NaHO produces a white precipitate of stannic hydrate, H_2SnO_3, or stannic acid, which is completely soluble in excess, forming potassium or sodium stannate, soluble in hydrochloric acid.

NH_4OH precipitates the hydrate; excess redissolves it but slightly. Tartaric acid prevents the precipitation.

Soluble carbonates give the same precipitate.

Stannic chloride furnishes an interesting case of precipitation—viz., by means of neutral salts, such as sodium sulphate, ammonium nitrate (in fact, most neutral salts). Metastannic acid, $H_{10}Sn_5O_{15}$, is precipitated on heating, provided the solution of stannic chloride is not too acid, thus:

$$5SnCl_4 + 20Na_2SO_4 + 15OH_2 = H_{10}Sn_5O_{15} + 20NaCl + 20NaHSO_4.$$
$$5SnCl_4 + 20NH_4NO_3 + 15OH_2 = H_{10}Sn_5O_{15} + 20NH_4Cl + 20HNO_3.$$

Metallic zinc precipitates from acid solutions of stannous or stannic chloride metallic tin in the form of grey laminæ, or of a spongy mass which can be readily dissolved in hydrochloric acid, especially when in contact with a piece of platinum foil. Metallic iron produces no precipitate but reduces to a stannous salt.

Metallic tin reduces stannic to stannous chloride, thus:

$$SnCl_4 + Sn = 2SnCl_2.$$

Copper similarly:

$$2Cu + SnCl_4 = SnCl_2 + Cu_2Cl_2.$$

A solution of stannous chloride (containing hydrochloric acid) ✓ cannot be kept, when exposed to air, without changing to stannic chlorides and insoluble stannous oxychloride, Sn_2OCl_2, on account of the great attraction which stannous salts possess for oxygen, thus:

$$(1)\ 2SnCl_2 + O = Sn_2OCl_2 + Cl_2.$$
$$(2)\ SnCl_2 + Cl_2 = SnCl_4.$$

Hence granulated metallic tin or pure tinfoil is usually put into stannous chloride solutions in order to prevent the oxidation, and an excess of free acid to prevent precipitation.

2. **ANTIMONY,** Sb''' and ^{v}.—This metal is sometimes found native; also in combination with oxygen as white antimony, Sb_2O_3, but more frequently as sulphide, Sb_2S_3 (grey antimony, stibnite), and in combination with other metallic sulphides (Ag_2S, PbS, Cu_2S), as sulphantimonite and sulphantimonate.

Metallic antimony is eminently crystalline and of a bluish-grey colour. Its atomic weight = 119·6; specific gravity, 6·71. Melts at 440° C., and boils between 1090 and 1450° C. It unites with most metals, forming hard and in most cases fusible alloys. It is, in fact, scarcely employed alone as a metal. It has also the effect of whitening its alloys when only present in small amount.

Owing to its strongly developed cystalline character, it is a very brittle metal; water and acids, with the exception of nitric, have little or no action at ordinary temperatures. It combines with oxgyen, sulphur, and the halogens directly, and with considerable energy, in two degrees, forming two distinct classes of compounds.

Antimonious compounds.		*Antimonic compounds.*	
$SbCl_3$,	Antimonious chloride.	$SbCl_5$,	Antimonic chloride.
Sb_2O_3,	„ oxide.	Sb_2O_5,	„ oxide.
Sb_2S_3,	„ sulphide.	Sb_2S_5,	„ sulphide.
$HSbO_2$,	Metantimonious acid.	$HSbO_3$,	Metantimonic acid.

Both these acids can enter into combination with strong bases, such as potash, or soda, to form weak salts—metantimonites and metantimonates, viz.:

$KSbO_2$, Potassium metantimonite.
$KSbO_3$, Potassium metantimonate.
$NaSbO_3$, Sodium metantimonate.

Sb_2O_4 is formed when antimonic oxide (obtained by the action of nitric acid upon antimony) is ignited. This compound is of some importance, as it serves for the quantitative estimation of antimony.

EXPERIMENTS.

I. Heated in air the metal melts readily and begins to give off white vapours, which condense on cooler parts of tube. A white crystalline oxide

forms on and surrounds globule of melted metal. It is Sb_2O_3, which fuses to a yellow mass and begins to sublime at a red heat.

II. Heated with sulphur, combination takes place easily, some of the product *subliming* to the upper part of tube by the heat evolved. The product is a reddish-black, especially the sublimate.

III. Hydrochloric acid has no action on the metal. Sulphuric, even when concentrated and hot, has only a very slow action.

Nitric oxidises the metal to a white amorphous powder containing Sb_2O_3 and Sb_2O_5, which is quite insoluble in nitric acid, but dissolves in some other acids and in soda.

Soda dissolves both the oxide produced as in I., or the sulphides as in II. The metal is unaffected by either soda or ammonia.

N.B.—If the melted globule obtained in I. be thrown out on to a large piece of paper it will break up, and the small globules will glow brightly and flow over the paper, leaving white *and* brown lines or streaks, partly oxide, partly metal, showing that both metal and oxide were in vapour.

DRY REACTIONS.

On heating metallic antimony or antimony mineral, *e.g.*, grey antimony, with free access of air, either on charcoal or in a glass tube open at both ends, dense white fumes of antimonious and antimonic oxides are given off, which condense on the colder part of the charcoal or glass tube, thus:

$$Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2.$$

All compounds of antimony can be reduced to the metallic state when heated on charcoal with sodium carbonate and potassium cyanide. A brittle globule of metallic antimony is obtained, giving off dense white fumes of Sb_2O_3 (even after the withdrawal of the metal from the flame), which thickly encrust the metallic globule with a network of brilliant acicular crystals.

This is sometimes difficult to bring about.

REACTIONS IN SOLUTION.

Chlorine and bromine attack antimony violently, forming with it $SbCl_3$ and $SbBr_3$, or $SbCl_5$ and $SbBr_5$, according to the proportions of halogen employed, and the temperature at which the combination takes place. Hydrochloric acid has no action upon the metal; but aqua regia dissolves it readily to $SbCl_5$. Nitric acid converts it into a compound containing Sb_2O_3 and Sb_2O_5, insoluble in nitric acid, soluble in tartaric acid. Grey antimony, Sb_2S_3, as well as Sb_2S_5, dissolves in concentrated hydrochloric acid with evolution of sulphuretted hydrogen, the latter sulphide with separation of sulphur.

Two distinct classes of compounds exist.

A. *Antimonious compounds.*—Antimonious chloride dissolved in a little HCl or tartar emetic, potassium antimony tartrate, also in dilute HCl, will give the under-mentioned reactions. There are scarcely any "salts" of antimony.

SH_2 (group-reagent) gives an orange-red precipitate of hydrated antimonious sulphide, Sb_2S_3, soluble in alkaline sulphides and in

potassium or sodium hydrate; reprecipitated by hydrochloric acid; slightly soluble in ammonium hydrate; all but insoluble in hydrogen ammonium carbonate and in hydrogen ammonium or hydrogen potassium sulphites. It dissolves in boiling concentrated hydrochloric acid.

Temperature and concentration of the reagents produce reciprocal effects.* In a dilute hydrochloric acid solution the $SbCl_3$ exchanges its chlorine in the cold for sulphur with SH_2, Sb_2S_3 being precipitated, whilst boiling concentrated hydrochloric acid dissolves Sb_2S_3 readily with evolution of SH_2.

$(NH_4)_2S$ produces the same precipitate as SH_2, soluble in excess.

KHO or NaHO precipitates antimonious oxide, Sb_2O_3, readily soluble in excess, with formation of potassium antimonite.

NH_4OH, same precipitate, almost insoluble in excess.

Soluble carbonates, the same precipitate.

OH_2 decomposes $SbCl_3$, forming a white insoluble basic salt, antimonious oxychloride, SbOCl, soluble in tartaric acid. (Distinction from bismuthous oxychloride, BiOCl.) Water, therefore, gives no precipitate with a solution of potassium antimonyl tartrate (tartar emetic) $C_2H_2(OH)_2 \begin{matrix} CO_2K \\ CO_2SbO \end{matrix}$; and alkalies and alkaline carbonates produce a partial precipitation only after some time.

Metallic Zn, Cu, Cd, Fe, Al, Sn, and Pb precipitate the metal in the absence of free nitric acid as a black powder. Some SbH_3 is liable to be formed.

A rather delicate reaction for antimony consists in precipitating the metal from a dilute hydrochloric acid solution on platinum foil or on the lid of a platinum crucible, by means of a small strip of metallic zinc. H and SbH_3 (antimoniettted hydrogen) are evolved, and the platinum is stained brown or black by the deposited metal. Mere traces of antimony can thus be discovered. The stain is little, if at all, affected by hot dilute hydrochloric acid, but disappears on heating with nitric acid. (Tin gives no *black stain* on platinum.) The finely divided metal, as precipitated by zinc, is more readily acted upon by acids than when in a compact state. This is a general property, however.

Compounds containing triad antimony exhibit a tendency (less marked, however, than in stannous compounds) to combine with more chlorine, &c., and to pass into antimonic compounds.

The following are some of the reactions naturally arising from this tendency of antimonious compounds:

When a current of chlorine gas is passed over solid $SbCl_3$,

* These are mostly mass reactions. The student's attention might have been drawn to them sooner. As a rule, perhaps when more is known, without exception, chemical reaction is a reversible cycle.

$$a \quad M'' + {}_nH_2O = H_2 + M''O + n - 1H_2O.$$
$$b \quad M''O + {}_nH_2 = M'' + H_2O + n - 2H.$$

For the completion of each of these equations, it requires that n must have a considerable value.

chlorine is absorbed; the trichloride liquefies, forming pentachloride:

$$SbCl_3 + Cl_2 = SbCl_5$$

Solid antimonious chloride — Liquid antimonic chloride.

Sodium metantimonite, $NaSbO_2$, is oxidised in the presence of sodium hydrate, by free iodine, with formation of sodium metantimonate, $NaSbO_3$ and NaI, thus:

$$NaSbO_2 + I_2 + 2\ NaHO = NaSbO_3 + 2NaI + OH_2.$$

A hydrochloric acid solution of $SbCl_3$ reduces $AuCl_3$ to metallic gold (frequently with separation of $HSbO_3$), thus:

$$3SbCl_3 + 2AuCl_3 = 3SbCl_5 + Au_2.$$

Sodium metantimonite is oxidised in an alkaline solution by argentic oxide, OAg_2, to sodium metantimonate, a lower oxide of silver or perhaps metallic silver * being formed, which is insoluble in ammonium hydrate, OAg_2, being readily soluble. (Distinction between Sb_2O_3 and Sb_2O_5.)

The several reactions may be expressed as follows:

$$(1)\ SbCl_3 + 4NaHO = NaSbO_2 + 3NaCl + 2OH_2.$$

(NaSbO₂ = Sodium metantimonite)

$$(2)\ 2AgNO_3 + 2NaHO = OAg_2 + 2NaNO_3 + OH_2.$$

(OAg_2 = Argentic oxide (insoluble in NaHO, soluble in NH_4OH))

$$(3)\ NaSbO_2 + 2OAg_2 = NaSbO_3 + OAg_4$$

(OAg_4 = Black argentous oxide (?) (insoluble in NH_4OH).)

$Na_2S_2O_3$ (sodium thiosulphate) precipitates Sb_2S_3, thus:

$$3Na_2S_2O_3 + Sb_2O_3 = Sb_2S_3 + 3Na_2SO_4.$$

B. *Antimonic compounds.*—Potassium metantimonate, $KSbO_3$, may conveniently be employed for studying the reactions in an aqueous solution.

This salt is prepared by fusing metantimonic acid, $HSbO_3$, with a large excess of KHO, in a silver crucible, or by deflagrating finely powdered metallic antimony with a mixture of potassium nitrate and carbonate in a porcelain crucible, and dissolving the mass in cold water.

* There is still some question as to the composition of these silver compounds, although a good deal of work has been done with them.

$HSbO_3$ fused with caustic soda gives sodium metantimonate, which is insoluble in water, or nearly so.

$KSbO_3$ is readily decomposed by concentrated acids (hydrochloric or nitric), metantimonic acid being precipitated. It dissolves in excess of warm dilute HCl.

SH_2 gives from a solution of $HSbO_3$ in excess of hydrochloric acid, an orange precipitate of antimonic sulphide, Sb_2S_5, mixed with Sb_2S_3 and S; soluble in alkaline sulphides, readily soluble in ammonium or potassium hydrate; also soluble in boiling concentrated hydrochloric acid, with evolution of SH_2 and deposition of S; only very sparingly soluble in cold hydrogen ammonium carbonate.

$(NH_4)_2S$, same precipitate, soluble in excess.

Ferrous sulphate does not reduce antimonic compounds.

Antimonic compounds, like stannic salts, can, under certain conditions, act as oxidising agents, *e.g.*:

On igniting antimonic anhydride, it splits up into Sb_2O_4 and oxygen.

$SnCl_2$ precipitates $HSbO_2$ from a hydrochloric acid solution of $HSbO_3$, the $SnCl_2$ being converted into $SnCl_4$.

On boiling a solution of $HSbO_3$ in hydrochloric acid, whereby some $SbCl_5$ is produced, with potassium iodide, iodine is liberated, colouring the solution brown. Iodine is set free because $SbCl_5$ on being heated with KI behaves thus: $SbCl_5 + 2KI = 2KCl + I_2 + SbCl_3$. The liberated iodine is readily recognised by means of the starch reaction.* (Distinction between antimonious and antimonic compounds.)

$SbCl_5$ is useful in a number of cases as a conveyer of Cl to organic bodies.

3. **ARSENIC**, As''' and ^{v}.—This body is very widely distributed in small quantities in nature in a state of combination. It is sometimes found native, but exists most frequently united with sulphur as realgar, As_2S_2, and as orpiment, As_2S_3, or arsenious sulphide (sulpharsenious anhydride); with metals it exists in arsenical nickel, As_2Ni, copper nickel, As_2Ni_2, and in smaltine, As_2Co. Arsenic acts generally more like a metalloid than a metal. Metallic arsenides are frequently found in combination with metallic sulphides, such as the sulphides of Ag, Fe, Ni, Co, Cu, &c., as in the common mineral mispickel, or arsenical pyrites, $FeAs_2$, FeS_2, in nickel glance or grey nickel ore, $NiAs_2,NiS_2$, and in cobalt glance, $CoAs_2,CoS_2$. Arsenic occurs also in the form of metallic arsenates, such as calcium, magnesium, nickelous, cobaltous, lead arsenates; for example, in the mineral pharmacolite, $Ca_2As_2O_7,6OH_2$ (calcium pyrarsenate), in nickel ochre, $Ni_3As_2O_8,9OH_2$, in cobalt bloom, $Co_3As_2O_8,8OH_2$, and in mimetesite, $3Pb_3As_2O_8,PbCl_2$.

Metallic arsenic is highly crystalline, of a dark grey colour, and exceedingly friable. Its atomic weight = 74·9; specific gravity, 5·73. It does not melt before volatilising at the ordinary pressure, but

* See test for iodine with starch paper or starch paste due to a supposed compound of iodine and starch.

under considerable pressure appears to melt at a red heat. It passes into vapour slightly at all temperatures and sublimes in crystals; distils readily at 449–450° C. It oxidises on exposure to air superficially, and also on contact with water slowly. Acids have no action upon it in the sense of forming salts. Nitric acid oxidises it to arsenic acid. Other substances containing oxygen also attack it. Alkalies dissolve it, hydrogen being liberated. It combines directly with sulphur and the halogens, in addition to oxygen, in two degrees, forming arsenious and arsenic compounds. All these compounds are volatile, mostly without decomposition. It alloys, or unites, with most other metals, and imparts hardness, fusibility and brittleness, even when in small quantity.*

Traces of arsenic are almost invariably found in commercial S, Fe, Cu, Zn, Sn, H, H_2SO_4, and HCl. On account of the solubility of its oxides, arsenic is found in some mineral waters and in the deposits from them.

Arsenic, as element, is scarcely employed, but a number of alloys contain it. Its compounds, both with oxygen and sulphur and salts of the acids it forms, are very largely used.

In its chemical nature it shows a strong resemblance to phosphorus and less distinctly to nitrogen.

EXPERIMENTS.

I. Heated in the tube (N.B. a very small particle only to be used), the metal gives off vapour, part of which is condensed on the upper cool end of tube. A white ring, and generally also a black or brown ring, is formed alongside, but nearer the heated part of tube. A very unpleasant odour is perceptible whilst the substance is vaporising. The white ring is generally crystalline, As_2O_3; it dissolves in hot water. The brown ring is dull and amorphous, and the black one is shining, but not distinctly crystalline.

II. Heated with sulphur a yellow-red substance is immediately formed which sublimes very easily from one part of tube to another. It is darker whilst hot than when cold. It is a sulphide, and may be As_2S_3, or As_2S_2.

III. Acids have no solvent action. Nitric acid oxidises it to As_2O_3 or As_2O_5, which dissolve slightly.

Ammonia has no action on the metal, but dissolves the oxide from I. or from III., and also the sulphide in II. Alkalies, KHO and NaHO, dissolve the metal with evolution of hydrogen; the oxides and sulphides also dissolve in alkaline solutions. The hydrogen evolved is not pure, but contains always some AsH_3; great care must be taken not to breathe this.

DRY REACTIONS.

Arsenic can be completely volatilised. When heated in contact with air, either on charcoal or in an open tube, it burns and forms arsenious anhydride, As_2O_3, which gives a peculiar fume and coloured flame and most characteristic odour.† Arsenical compounds give the same indications when heated by themselves on charcoal in the

* The effect of arsenic in small quantity on metals is probably due to the formation of *arsenides*, which are then retained on the excess of metal as a sort of solid solution.

† The odour of arsenic vapour is said to resemble that of garlic. They are *somewhat* alike.

reducing flame, and on the addition of sodium carbonate and potassium cyanide, whether the arsenic be present as arsenite or arsenate. The blowpipe experiments should be performed with great caution, since arsenical fumes are poisonous. The reaction being so very

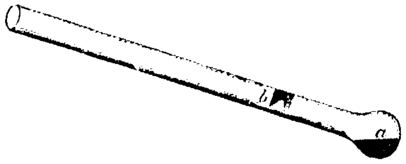


FIG. 8.

delicate very small quantities only of the substance need or should be operated upon.

When arsenical compounds are heated in a bulb tube, Fig. 8 or 9, mixed with a proper reducing agent (such as sodium carbonate and charcoal powder or black flux),* metallic arsenic sublimes and is deposited in the shape of a lustrous steel-grey mirror, *b*, in the upper part of the tube.

As_2O_3, and some arsenites, when heated with a carbonate as $CaCO_3$, calcium carbonate, or K_2CO_3 or Na_2CO_3, give a sublimate of metallic arsenic along with some oxide. The whole of the arsenic present as arsenite is not given off.

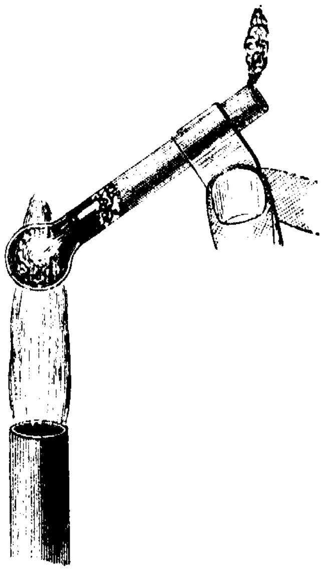


FIG. 9.

REACTIONS IN SOLUTION.

Chlorine attacks arsenic violently, forming a highly poisonous and volatile liquid, arsenious chloride, $AsCl_3$. Hydrochloric acid does not act upon arsenic; nitric acid oxidises it to arsenious and arsenic acids, according to the concentration of the acid.

Arsenic forms two oxides, sulphides, &c., and two well characterised series of salts, arsenites and arsenates, as well as arsenides.

* See Reagents, Appendix. This reagent should be a mixture of *dry* soda-lime and charcoal in fine powder. It then answers for Hg, NH_4, As, and Cd compounds. Black flux, made by igniting Rochelle salt, is still better as a reducing agent.

A. *Arsenious compounds.*—A solution of arsenious anhydride, As_2O_3, in dilute hydrochloric acid, or an aqueous solution of an arsenite, K_3AsO_3 (potassium arsenite), will give the reactions.

SH_2 (group-reaction) produces in an acid solution, especially on gently heating, a lemon-yellow precipitate of arsenious sulphide, As_2S_3, readily soluble in caustic alkalies, in alkaline carbonates and sulphides, forming alkaline arsenites and sulpharsenites; it is reprecipitated from any of these solutions on the addition of dilute hydrochloric or other acid. It is almost insoluble in concentrated hydrochloric acid even on boiling; but soluble in nitric acid. On digesting freshly precipitated arsenious sulphide in a solution of hydrogen potassium sulphite, $HKSO_3$, with excess of sulphurous acid, the yellow precipitate is dissolved, and the solution contains potassium metarsenite and potassium thiosulphate, after driving off the excess of sulphurous acid by evaporation, thus:

$$2As_2S_3 + 16HKSO_3 = 4KAsO_2 + 6K_2S_2O_3 + S_3 + 7SO_2 + 8OH_2.$$

$(NH_4)_2S$, same precipitate, soluble in excess.

$AgNO_3$ produces from a solution of a neutral arsenite, or from a solution of As_2O_3 in water, rendered neutral by cautiously adding ammonium hydrate, a yellow precipitate of silver arsenite, Ag_3AsO_3, readily soluble in ammonium hydrate, ammonium chloride or nitric acid. The ammoniacal solution of Ag_3AsO_3 and OAg_2, is decomposed on boiling, with separation of metallic silver and formation of silver arsenate, Ag_3AsO_4, thus:

Ag_3AsO_3	+	OAg_2	=	Ag_3AsO_4	+	Ag_2.
Soluble in NH_4OH		Soluble in NH_4OH		Soluble in NH_4OH		Black precipitate

$CuSO_4$ produces a characteristic yellowish-green precipitate of hydrogen cupric arsenite, $HCuAsO_3$ (Scheele's green), from a solution of tripotassium arsenite, readily soluble in ammonium hydrate, ammonium chloride, or nitric acid.

Magnesium sulphate gives no precipitate in the presence of ammonium chloride.

Reinsch's test.—Arsenious oxide and most of its compounds dissolve in HCl, especially when concentrated, $AsCl_3$ being formed. On placing a perfectly clean piece of metallic copper into this solution and warming, a grey deposit forms on the copper. This consists of arsenic or a compound of As and Cu; Cu_5As_2. In a concentrated solution the deposit may be black in colour, and will peel off from the copper surface. Antimony is precipitated under similar conditions, so it is necessary to confirm this indication by taking the piece of copper which has become coated by the supposed arsenic film out of the acid solution, drying it by gentle pressure between blotting-paper, and then introducing into a perfectly dry test-tube, and gently heating over a lamp. If arsenic is present a sublimate of arsenious oxide in white crystals will form in the cooler portions

of the tube. In the case of large quantities some arsenic will sublime unoxidised, and form a brilliant black or brown film on the glass surface.

Arsenious compounds exert a powerful reducing action, when brought in contact with bodies capable of parting with oxygen, chlorine, &c. This property is more marked in arsenious than in antimonious compounds.

$AuCl_3$ (auric chloride) produces from an acid solution of As_2O_3 a precipitate of metallic gold, and the reaction is so exact * that the amount of arsenic can be determined quantitatively from the weight of the precipitated gold:

$$4AuCl_3 + 3As_2O_3 + 15OH_2 = 6H_3AsO_4 + 4Au + 12HCl.$$

Chlorine water or compounds capable of yielding chlorine, such as a solution of bleaching powder, or of sodium hypochlorite, NaOCl (Eau de Javelle), oxidise As_2O_3 rapidly, thus:

$$As_2O_3 + 2Cl_2 + 5OH_2 = 2H_3AsO_4 + 4HCl.$$

Iodine, dissolved in a solution of potassium iodide, converts a solution of As_2O_3 in excess of hydrogen sodium carbonate into As_2O_5, with formation of an alkaline iodide, thus:

$$HNa_2AsO_3 + 2HNaCO_3 + I_2 = HNa_2AsO_4 + 2NaI + OH_2 + 2CO_2.$$

Chlorine, iodine, and bromine act as oxidising agents by decomposing water or a metallic oxide or hydrate. They form, with the hydrogen, HCl, HI, HBr, or with a metal the corresponding haloïd salt, and the oxygen is transferred to the As_2O_3.

Cupric oxide, or cupric salts, in the presence of potassium hydrate also oxidise. On adding to a strongly alkaline solution of tripotassium arsenite *a few drops of cupric sulphate, and warming gently*, the blue solution deposits a red precipitate of cuprous oxide, Cu_2O, and leaves tripotassium arsenate, K_3AsO_4, in solution. (Distinction between As_2O_3 and As_2O_5).

The deoxidising action which arsenious compounds exert upon the higher oxides of chromium and manganese has already been described. (See Chromium and Manganese.)

B. *Arsenic compounds.*—An aqueous solution of tripotassium arsenate K_3AsO_4, is employed.

SH_2 gives scarcely any precipitate from an acidulated solution

* All chemical reactions are of course *exact* under proper conditions. Where a reaction is spoken of as *partial*, either the physical conditions are not completely known, or more than one path is open for the chemical action to proceed along, and under one condition of temperature it may run more in one direction than another. In many known cases reactions can be reversed by a considerable change of temperature.

of K_3AsO_4, until the solution is heated, and a current of gas passed through for some time. It is difficult to effect complete precipitation even then. The precipitate consists of arsenious sulphide and sulphur. It is preferable to reduce the As_2O_5 first to As_2O_3, by a more powerful reducing agent than SH_2, for example by sulphurous acid: $K_3AsO_4 + H_2SO_3 = K_3AsO_3 + H_2SO_4$, after which sulphuretted hydrogen precipitates the arsenic readily as arsenious sulphide.

$AgNO_3$ gives a reddish-brown precipitate of triargentic arsenate, Ag_3AsO_4, soluble in ammonium hydrate and in nitric acid.

$CuSO_4$ produces a pale greenish-blue precipitate of hydrogen cupric arsenate, $HCuAsO_4$, soluble in ammonium hydrate and nitric acid.

$MgSO_4$ in the presence of ammonium chloride and ammonium hydrate, gives a white crystalline precipitate of ammonium magnesium arsenate, NH_4MgAsO_4. (Distinction of As_2O_5 from As_2O_3.)

Fe_2Cl_6 gives a yellowish-white precipitate of ferric arsenate, $Fe_2(AsO_4)_2$.

Lead acetate gives a white precipitate of lead arsenate, $Pb_3As_2O_8$.

$(NH_4)_2MoO_4$ (ammonium molybdate) with excess of nitric acid, gives a yellow precipitate of ammonium arseno-molybdate. This precipitate closely resembles the phosphate one.

Metallic copper does not precipitate metallic arsenic from dilute acid solutions of As_2O_5; but on adding concentrated hydrochloric acid, and heating, a grey film of As_2Cu_5 is obtained. (Distinction between As_2O_3 and As_2O_5.) Some chlorine is liberated and then attacks the Cu forming copper chloride.

Arsenic as well as arsenious compounds are capable of oxidising some other bodies, and become themselves reduced either to a lower stage of activity or to arsenic.

Sulphurous acid reduces arsenic acid to arsenious acid.

Sodium thiosulphate deprives arsenious acid of its oxygen, and converts it into As_2S_3, thus:

$$2As(HO)_3 + 3Na_2S_2O_3 = As_2S_3 + 3Na_2SO_4 + 3OH_2.$$

As_2O_3 or As_2O_5 can be detected in solution by the reducing action of hypophosphorus acid, HPO_2, along with SO_2 the arsenic becoming As_2S_3.

To the arsenic solution one or two drops of PCl_3 (or a little PI_3), or hypophosphorus acid itself, is added and then a few bubbles of SO_2 gas sent through. On warming a yellow precipitate of As_2O_3, sometimes with a little sulphur, appears.

Carbon at a red heat removes the oxygen from both oxides of arsenic.—A fragment of arsenious anhydride (white arsenic) is placed in the pointed end, *a*, of a hard glass tube drawn out before the blowpipe, as seen in Fig. 10. A splinter of well dried charcoal is next placed in the narrow part of the tube at *b*, somewhat above the fragment of the arsenical compound. This charcoal is heated over a gas flame or the flame of a spirit lamp. When the charcoal is well ignited a second

flame is applied to the lower end of the tube, in order to volatilise the arsenical compound, the vapour of which, on passing over the glowing charcoal, is deprived of its oxygen, and metallic arsenic is deposited in the form of a shining black mirror on the inside of the tube, above the charcoal at *c*. The end reaction may be:

$$2As_2O_3 + 6C = As_4 + 6CO_2.$$

This test is very delicate. Arsenic, in arsenites or arsenates, is liberated by mixing perfectly dry charcoal powder, or soda-lime charcoal, with the dry substance previous to its introduction into the tube, which may have a small bulb blown at its lower end. The sublimation of metallic arsenic is accompanied by the characteristic garlic-like odour.

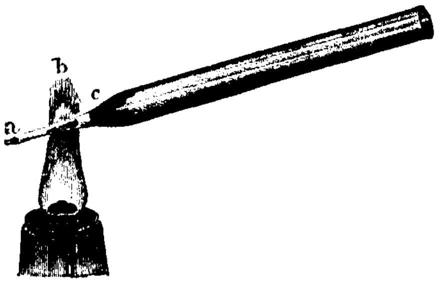


FIG. 10 (½).

KCy reduces arsenical compounds — oxides as well as sulphides—with formation of potassium cyanate or sulphocyanate. A mixture of potassium cyanide with the arsenical compound is heated in a bulb tube, *a* (Fig. 11). Metallic arsenic is deposited at *b*.

The changes are expressed as follows:

$$As_2O_3 + 6KCy = 6KCyO + As_4.$$
Potassium cyanate

$$2As_2S_3 + 6KCy = 6KCyS + As_4.$$
Potassium sulphocyanate

But since commercial potassium cyanide contains potassium cyanate, as well as potassium carbonate (its composition may be expressed as $5KCy + KCyO + xK_2CO_3$), a portion only of the arsenic in As_2S_3 is obtained in the metallic form, and a sulpharsenate is formed which is not reduced by potassium cyanide. On mixing the arsenious sulphide with sulphur, the whole of the arsenic remains behind in the fused mass, as sulpharsenate, and no metallic deposit is obtained. (In the presence of sulphides of Pb, Cu, Ag, Au, Ni, Co, Fe—as, *e.g.*, of FeS_2 in arsenical pyrites, NiS_2, in nickel glance—which are reduced to the metallic state by the action of potassium cyanide, scarcely any arsenical mirror is obtained, because the liberated metallic arsenic would

FIG. 11.

immediately alloy itself with the metals, a portion only of the arsenic being liberated.) These changes are expressed by the equations—

(1) $5As_2S_3 = 3As_2S_5 + As_4$.
(2) $4As_2S_5 + 12K_2CO_3 = 5K_3AsS_4 + 3K_3AsO_4 + 12CO_2$.

The reduction is conveniently effected by mixing dry arsenious sulphide with one part of potassium cyanide and three parts of sodium carbonate, and introducing the mixture into a piece of combustion tube *c*, drawn out to a capillary tube as in Fig. 12. A slow current

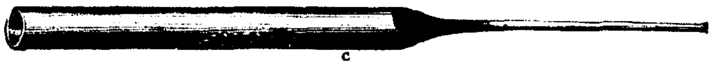


Fig. 12.

of carbonic anhydride generated from marble and hydrochloric acid in the flask A, Fig. 13, and dried by passing through *b* into the flask B, containing concentrated sulphuric acid, and through the delivery tube *c*, over the mixture in tube C, heated at first gently, till all the moisture has been driven out, and then strongly, almost to fusion—when a mirror of metallic arsenic collects in the neck of the drawn-out tube.

The reaction has this advantage, that no antimony mirror is obtained in the same way.

In order, however, to avoid missing the arsenic, either altogether or obtaining only a portion of it, as stated above, it is preferable to

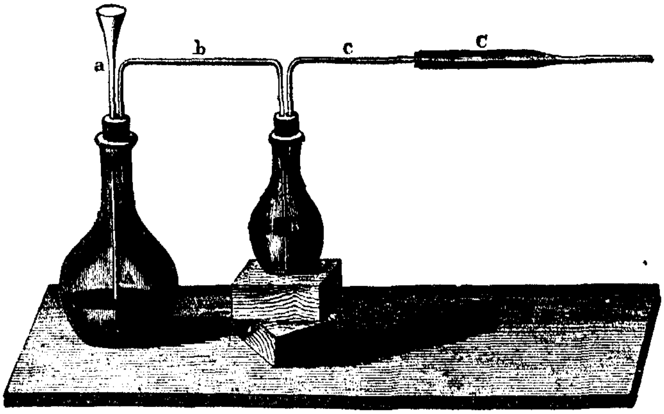


Fig. 13.

treat the arsenious sulphide with a few drops of concentrated nitric acid, and to evaporate with a little sulphuric acid (in order to decompose any metallic nitrates, if present). The sulphuric acid is

next neutralised with sodium carbonate, and the mass thoroughly dried before mixing it with potassium cyanide, and reducing as described. The fused mass retains the antimony, and a good arsenical mirror is obtained, provided no lead, copper, or other reducible metals are present.

MARSH'S TEST.

Arsenious and arsenic acids are both reduced by nascent hydrogen, which combines with the oxygen of the arsenical oxides to form water, whilst the arsenic in its nascent state, or the very moment it is liberated from the oxygen, also combines with hydrogen to form a gaseous compound of arsenic, called arsenietted hydrogen (arsenious hydride)—AsH_3. This gas is obtained nearly pure by acting with dilute sulphuric acid upon an alloy or compound of zinc and arsenic (Zn_3As_2). The zinc takes the place of hydrogen in the acid, and arsenious hydride is liberated, thus:

$$As_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3.$$

Some other arsenides act in a similar manner. Sodium arsenide decomposes on contact with water liberating AsH_3, and also forming

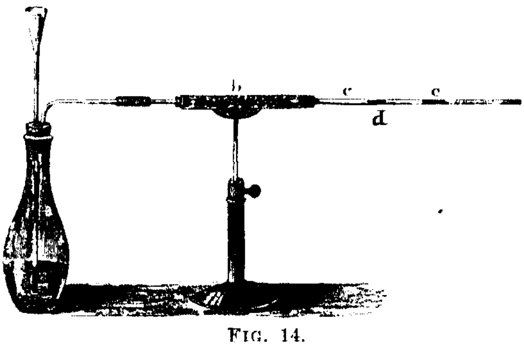


FIG. 14.

some As_2H_4, a brownish solid. Too great care cannot be taken with these arsenic compounds.

Arsenious hydride is an exceedingly poisonous gas, and the student must on no account attempt to prepare it pure. Its properties, for qualitative purposes, may be studied equally well in a mixture of the gas with much hydrogen.

All experiments with it must be conducted in a fume chamber where a good indraught of air can be obtained. Arsenious hydride possesses a very nauseous odour, and burns with a peculiar livid bluish flame when the jet of hydrogen containing it is lighted. This is due to the combustion of arsenic to As_2O_3.

Generate hydrogen in a flask, *a*, Fig. 14, from pure zinc (free from

arsenic) and pure dilute sulphuric acid. Dry the gas by passing it over calcium chloride and connect the drying tube, *b*, with a piece of hard glass tubing, *c*, drawn out to a jet. The hydrogen gas may be ignited at the jet, as soon as it has displaced the air in the generating flask, *a*, and drying tube, *b*. It burns with an almost colourless flame if the zinc and acid be pure. On introducing a few drops of an arsenious or arsenic solution * through the funnel-tube, the flame is seen to change to blue, and on holding a piece of porcelain (*e.g.*, a dish, or the lid of a porcelain crucible) into the flame, a black mirror or deposit of metallic arsenic is obtained. Or the metal may be collected—by heating the glass tube through which the hydrogen passes—in the form of a metallic ring, *d*, which deposits within the tube immediately in front and in rear of the spot where the glass is heated. The hydrogen should not be generated too rapidly, if a good ring is to be obtained.

Several arsenical mirrors may be obtained if a long piece of narrow

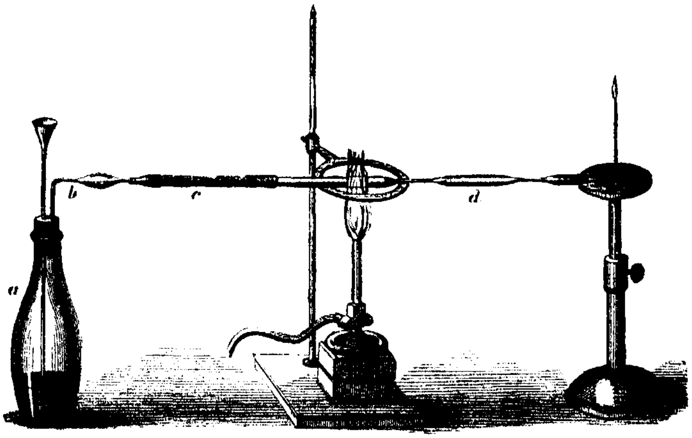


FIG. 15.

combustion tube, Fig. 15, be employed, which has been contracted in several places by drawing it out in the flame of a blowpipe. Arsenious hydride is generated in the flask, *a*, and passing through *b*, the drying tube, *c*, and combustion tube, *d*, issues from the drawn-out jet, where it can be burnt. The tube, *d*, is heated in one or in several places, just before the several drawn-out narrow parts. An arsenical mirror is obtained a little beyond the heated part of the tube, as seen in Fig. 15. Little or no arsenious hydride need thus escape from the jet, especially if a slow current of hydrogen be generated.

* Any considerable excess of oxidising agents, such as nitric acid, chlorine, &c., should be avoided. The same holds good for the preparation of SbH_3.

The deposition of arsenic in the tube arises from the decomposition of the arsenious hydride, which, at a high temperature, is broken up into arsenic, which is deposited, and hydrogen which passes on and burns at the jet. The decomposition which takes place when a cold piece of porcelain is lowered into the flame, is readily explained, if it be remembered what takes place when some cold porcelain is held in a candle or gas flame. A deposit of soot is obtained (finely divided carbon from the hydrocarbons), because the combustion is disturbed, and the temperature of the flame suddenly lowered. The gas can only burn where it is in contact with the air—*i.e.*, on the outside. The arsenious hydride on passing through the inner portion of the flame, is decomposed by the heat into arsenic vapour and hydrogen gas: the latter escapes through the outer portion of the flame, and is burnt, arsenic being deposited on the cold porcelain surface. The decomposition of arsenious hydride takes place, even if very little of the gas is mixed with much hydrogen gas. Marsh's test is, therefore, extremely delicate.

It is *absolutely necessary* that both zinc and sulphuric acid be tested first. This is done by generating hydrogen, and allowing the gas to escape by itself for some time through the ignited combustion tube.

Care should also be taken to avoid introducing nitric acid, since *arsenious hydride is readily decomposed by this acid. It is therefore* preferable to dissolve arsenical compounds in hydrochloric acid, with the addition of a few small crystals of potassium chlorate, and to heat gently till no more chlorous odour is observable.

The metal antimony forms with nascent hydrogen a combustible gas analogous to arsenious hydride, called antimonietted hydrogen (antimonious hydride), SbH_3. It is prepared, though not in a pure condition, by acting with dilute sulphuric or hydrochloric acid upon an alloy of zinc and antimony, thus:

$$Sb_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2SbH_3.$$

It is obtained mixed with much hydrogen by introducing into a hydrogen apparatus a few drops of an antimony solution ($SbCl_3$, $KSbO_3$, or tartar emetic). The greater part of the antimony, however, remains behind, precipitated as metal, with perhaps some solid hydride Sb_2H_4 on the zinc. The hydrogen flame turns at once bluish-green, and white fumes of antimonious oxide, Sb_2O_3, ascend into the air. The gas has no particular odour, but is decidedly poisonous. On depressing a cold piece of porcelain into the flame, metallic antimony is deposited, and on heating the combustion tube, as in the case of the arsenic experiment, the gas is likewise decomposed into metallic antimony, which collects in the narrowed portions of the tube and forms a dull black mirror, and hydrogen, which escapes and can be burnt at the jet.

Since both arsenic and antimony produce a metallic mirror, such mirror may be due to either metal or to a mixture of the two metals (in which case, however, the more volatile arsenic is deposited further

Heated in a tube either in air or vacuum it melts without change. A piece of gold leaf will melt into the glass of a test tube. When looked at it is yellow, when looked through it appears green.

II. Sulphur has little or no action on pure gold, but gold leaf generally becomes a little duller.

III. Single acids, as HCl, HNO_3, H_2SO_4, have no action.

KHO and NaHO have no action either in solution or when fused.

A mixture of HCl and HNO_3, which evolves chlorine or nitrosyl chloride, dissolves it, forming a yellow solution of $AuCl_3$, which on very careful evaporation leaves a yellow deliquescent solid.

On moderately heating chlorine is evolved, and metallic gold left.

DRY REACTIONS.

When heated on charcoal with sodium carbonate and borax in the reducing flame, gold compounds yield a yellow, very malleable globule of metallic gold.

To detect gold in argentiferous minerals in which it is present only in minute quantities, and associated with large quantities of other non-volatile metals, the powdered mineral is fused with borax and metallic lead, and the metallic "button" cupelled, as will be described under silver. The globule of white metal which is left on the cupel is beaten out, and the silver dissolved by digesting with a little nitric acid. The silver nitrate is poured off, and the gold washed with distilled water. The black insoluble residue is once more fused on charcoal before the blowpipe, when it assumes the well-known appearance of fine gold.

Old, and sometimes now, silver coins frequently contain a small quantity of gold, which, on dissolving in nitric acid, is left as a black powder.

When an insufficient quantity of silver is present in the "button" (see above) (which may be inferred from its pale-yellow colour), from two or four times its own weight of silver should be fused up with it, and the button so obtained beaten out and then treated with nitric acid in order to separate or "part" the gold.—Method of assaying gold.

REACTIONS IN SOLUTION.

Gold when unalloyed is soluble with ease in aqua regia only, forming a solution of auric chloride, $AuCl_3$, which may be employed for studying the reactions in solution.

SH_2 (group-reagent) gives from a cold solution a black precipitate of auric sulphide, Au_2S_3, from a boiling solution a brownish precipitate of aurous sulphide, Au_2S. These precipitates are insoluble in hydrochloric and nitric acids, but dissolve in aqua regia. They are likewise insoluble in normal ammonium sulphide, but soluble, although with difficulty, in the yellow sulphide, more readily in yellow sodium sulphide, with which they form a sulphosalt, Na_3AuS_3.

$(NH_4)_2S$ and sodium thiosulphate, same precipitate.

KHO or NaHO produces no precipitate.

NH_4OH produces from a concentrated solution of auric chloride

a reddish-yellow precipitate of ammonium aurate or fulminating gold, $(NH_3)_2Au_2O_3$, thus:

$$2AuCl_3 + 8NH_4OH = (NH_3)_2Au_2O_3{}^* + 6NH_4Cl + 5OH_2.$$

The detection of gold is attended with no difficulty, owing to the facility with which its compounds generally are reduced to the metallic state. Gold has little affinity for non-metallic elements; the compounds which it forms with them are readily broken up by heat alone, or on being brought into contact with bodies which have more affinity for the metalloids, leaving metallic gold in a finely divided condition as a brown powder, which acquires metallic lustre when dried and rubbed in a mortar. Hence auric chloride is a powerful oxidising agent, as has already been seen under tin, antimony, and arsenic. The *same oxidising action is called into play*, when $AuCl_3$ comes together with solutions of sulphurous and oxalic acid, ferrous sulphate, or chloride, cuprous chloride, dissolved in hydrochloric acid, mercurous nitrate, potassium nitrite, sugar in an alkaline liquid, and many other organic substances (*e.g.*, the epidermis); arsenious, antimonious, and phosphorous hydrides, and even free hydrogen decompose $AuCl_3$.

The following equations express these changes:

(1) $2AuCl_3$, *when ignited splits up into* $Au_2 + 3Cl_2$.
(2) Au_2S_3 " " $Au_2 + S_3$.
(3) $2AuCl_3 + 3H_2SO_3 + 3OH_2 = Au_2 + 3H_2SO_4 + 6HCl$.
(4) $2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6CO_2 + 6HCl$.
(5) $2AuCl_3 + 6FeCl_2 = Au_2 + 3Fe_2Cl_6$.
(6) $2AuCl_3 + 4FeSO_4 + OH_2 = Au_2 + Fe_2Cl_6 + Fe_2(SO_4)_3 + H_2SO_4$.
(7) $2AuCl_4 + 3Cu_2Cl_2 = Au_2 + 6CuCl_2$.
(8) $2AuCl_3 + 3Hg_2(NO_3)_2 = Au_2 + 3Hg(NO_3)_2 + 3HgCl_2$.
(9) $2AuCl_3 + 3KNO_2 + 3OH_2 = Au_2 + 3KNO_3 + 6HCl$.
(10) $2AuCl_3 + 2AsH_3 + 3OH_2 = Au_2 + 2H_3AsO_3 + 6HCl$.
(11) $2AuCl_3 + SbH_3 = Au_2 + SbCl_3 + 3HCl$.

In the analysis of a solution containing gold, it is usual to remove the gold in the metallic state, by boiling with oxalic and hydrochloric acids, before passing SH_2. The precipitated gold is collected on a filter and fused into a button on charcoal.

There are several other metals also in this group which are removed similarly before continuing the analysis.

Gold is precipitated from a hydrochloric acid solution, of $AuCl_3$ by most metals, even by Pt, Ag, and Hg.

PLATINUM, Pt″ and iv.—This metal is found native, but more frequently alloyed with other metals. The colour of platinum is somewhat between that of tin and silver, being whiter than tin but not so white as silver, or nearly so brilliant. It has about the same hardness as copper, and is eminently ductile and malleable, but somewhat inferior to gold in the latter property. Its atomic weight = 194; specific gravity, 21·50. Melting point between 2000° and

* This substance is explosive when dry. It may be a salt of auric acid or a hydrated amino compound.

2200° C. It is much less readily acted upon than gold, either by halogens or acids, and does not amalgamate with mercury. It is acted upon by fused caustic alkalies (NaOH and KOH). It is a bad conductor of heat and electricity. It forms two well characterised series of salts. It is characterised by its infusibility before the blowpipe, and is not acted upon by the usual fluxes. Sulphur has a slight action on platinum when not heated much more than about 500°. Se, Te and P act very rapidly, and nearly all metals melt with it readily. Some, as Na, Sn, As, Sb, Pb, &c., attack it vigorously, forming very fusible compounds or alloys. Its reactions in solution need, therefore, only be examined.

Unalloyed platinum is not attacked by either nitric, hydrochloric or sulphuric acid, but by aqua regia, with formation of platinic chloride, $PtCl_4$.* The action is slower than with gold. A solution of this salt is employed for studying the reactions of platinum.

SH_2 (group-agent) produces slowly a dark brown precipitate of platinic disulphide, PtS_2. On heating, the precipitate forms quickly. It is insoluble in nitric or hydrochloric acid, soluble in aqua regia, difficultly soluble in normal ammonium sulphide, more speedily in the yellow sulphide, with which it forms a sulpho-salt, $(NH_4)_2PtS_3$. Heated out of contact with air, it is decomposed into PtS and S.

$(NH_4)_2S$, same precipitate.

NH_4Cl produces a light-yellow crystalline precipitate of ammonium platinic chloride, $2NH_4Cl,PtCl_4$. From dilute solutions a precipitate is obtained only after evaporation to dryness (on a water-bath). The precipitate is somewhat soluble in water, insoluble in alcohol. (See Ammonia, *ante.*)

KCl produces a yellow crystalline precipitate of potassium platinic chloride, $2KCl,PtCl_4$, analogous in its appearance and properties to the precipitate just described. (See Potassium, *ante.*)

NaCl forms with platinic chloride a double chloride, which is, however, soluble in water, and is obtained in needle-shaped crystals by evaporation.

The precipitate produced by platinic chloride with NH_4Cl and KCl serves for the detection and isolation of platinum, and *vice versâ*, for the detection of ammonium or potassium compounds. (*Comp.* chapter ii.)

$PtCl_4$ is useful on account of the compounds which it forms with the chlorides of the alkali metals and with the chlorides of many organic bodies, *e.g.*, the so-called alkaloids, such as quinine, nicotine, &c., and amido bodies or bases generally.†

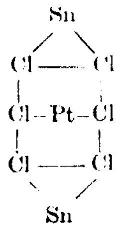
* When alloyed with silver, zinc, cadmium, and some other metals, and these alloys are treated with nitric acid, some platinum is dissolved along with the other metals. The amount dissolved varies with the metal, and the amount of platinum in the alloy.

† That is, compounds in which the group NH_2 is combined with a more or less complex carbon compound. The double salts with $PtCl_4$ are very characteristic bodies. Whether they arise from the energy of the platinum atom or are a consequence of a rise in valency on the part of the halogen is not yet

Platinum is capable of forming a lower chloride, platinous chloride, "Pt"Cl_2. This salt is obtained by heating platinic chloride for some time in an air or oil-bath up to 204° C., as long as any chlorine is evolved; or by acting with sulphurous acid upon a solution of platinic chloride, until the latter ceases to give a precipitate with ammonium chloride. $PtCl_2$ is a *greenish-grey powder, insoluble in water*, but soluble in hydrochloric acid.

Several reactions for platinum in solution are based upon the power which its salts possess of oxidising other bodies which are chemically unsaturated; but as platinic salts are not so easily reduced as gold salts, a solution of the latter metal is generally preferred. After what has been stated under gold, the following reactions will be readily understood:

$PtCl_4$ produces with $SnCl_2$ only a dark brownish-red colour, owing to the reduction of the platinic to platinous chloride and formation of a platinous tin chloride, $PtCl_2 2SnCl_2$ =



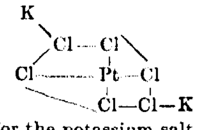
$PtCl_4$ is reduced by $FeSO_4$ only after long-continued boiling.

$PtCl_4$ is reduced to platinum by formic acid, HCO_2H, on heating, if the free acid be neutralised with sodium carbonate.

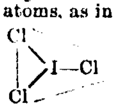
Metallic zinc precipitates metallic platinum.

$PtCl_2$ is very readily reduced to metallic platinum by $FeSO_4$ and other reducing agents, as oxalates, and is used in photography for this reason.

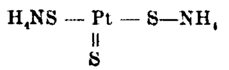
clearly settled. $PtCl_4$ is difficult to get perfectly pure. The ordinary solution is acid, and probably consists of $PtCl_4 2HCl$ chloroplatinic acid. A constitution as represented by the plan



is not at all unreasonable for the potassium salt, as there is plenty of evidence of the halogens acting as triad atoms, as in ICl_3 and many other cases.



The compound (page 104) $(NH_4)_2PtS_3$ is also probably of a similar type as these chloroplatinates:



$PtCl_2$ is soluble in $PtCl_4$ solution, and gives it a very dark colour, and also forms double salts with $SnCl_2$, &c.

Whenever platinum and gold are contained in a solution together with other metals of Group II., it is preferable to remove the gold, by means of oxalic acid (which does not reduce platinic chloride), before removing the platinum by evaporation with ammonium chloride.

Separation of the metals arsenic, antimony, and tin, whose *sulphides are soluble in yellow ammonium sulphide, or in* sodium hydrate.

The precipitate produced by the group-reagent is soluble in yellow ammonium sulphide, or in sodium hydrate, and may consist of three sulphides. If the precipitate be of a dark brown colour, stannous sulphide is indicated. If it be of a fine lemon-yellow colour, the presence of arsenious or stannic sulphide, and if orange-coloured, antimony.

The three sulphides are unequally soluble in hydrogen ammonium carbonate. As_2S_3 dissolves freely, SnS_2 very slightly, and Sb_2S_3 is all but insoluble. On digesting, therefore, the precipitate with hydrogen ammonium carbonate and filtering, arsenic is obtained in the filtrate, and the antimony and tin are left in the residue. In order to separate the remaining two metals, the antimony may be partly converted into antimonious hydride—tin does not form a gaseous compound with hydrogen. For this purpose the two sulphides are dissolved in hydrochloric acid well boiled to expel SH_2, and the solution of the mixed chlorides introduced into a Marsh's apparatus. Antimony is detected by the metallic deposit which antimonious hydride gives on porcelain, insoluble in NaOCl. Tin with some of the antimony is found in the generating flask deposited on the strips of zinc as a greyish-black metal. It is removed from the undissolved zinc, dissolved in hot hydrochloric acid (by the aid of a little platinum foil), and the solution tested with mercuric chloride. A white precipitate of mercurous chloride, Hg_2Cl_2, indicates the presence of tin.

The separation of arsenic, antimony, and tin, may thus be based upon—

1st. The solubility of As_2O_3 in hydrogen ammonium carbonate.
2nd. The formation of antimonious hydride.
3rd. The precipitation of tin by metallic zinc.

Several other methods of recognising and separating the metals tin, antimony, and arsenic, will readily suggest themselves, such as the one which is based upon:

1st. The precipitation of arsenic and antimony in the form of sulphides, by boiling a hydrochloric acid solution of the three metals with sodium thiosulphate, tin remaining in solution.

2nd. By boiling the precipitated As_2S_3 and Sb_2S_3 with hydrogen potassium sulphite and sulphurous acid; As_2S_3 is converted into potassium metarsenite, Sb_2S_3 remains undissolved.

A third method consists in:

1st. Removing the As_2S_3 by boiling with hydrogen ammonium carbonate.
2nd. Solubility of SnS in oxalic acid, Sb_2S_3 being insoluble.

Dissolve the sulphides of tin and antimony in a little strong hydrochloric acid, with the addition of a crystal of potassium chlorate, evaporate the solution till free from chlorine, make it slightly alkaline with caustic soda, and add a cold strong solution of oxalic acid, when the white precipitate thrown down by the soda easily redissolves. Pass sulphuretted hydrogen through the solution till no more antimony sulphide comes down; filter, and wash the precipitate with sulphuretted hydrogen water. Add to the filtrate some dilute hydrochloric acid, and pass sulphuretted hydrogen for some time; a yellow precipitate indicates the presence of tin.

A fourth method of recognising arsenic, antimony, and tin is based upon:

The introduction of a solution (in HCl by the aid of $KClO_3$) of the three sulphides into a hydrogen apparatus, and passing the evolved arsenious and antimonious hydride through a solution of silver nitrate; the tin remains behind precipitated on the zinc.
The solubility of the precipitated $SbAg_3$, in tartaric acid, and precipitation of the antimony by means of sulphuretted hydrogen from a hydrochloric acid solution.
The precipitation of the Ag_3AsO_3 from the silver nitrate solution by means of ammonia.

A fifth method of recognising the metals of group IIB, depends upon:

1st. The insolubility of As_2S_3 in strong hydrochloric acid, Sb_2S_3, SnS, and SnS_2 being dissolved. The presence of arsenic is confirmed by fusion with potassium cyanide and sodium carbonate.
2nd. The precipitation of the antimony on platinum by means of a strip of metallic zinc; a black stain indicates antimony.
3rd. Dissolving the tin precipitated on the zinc in warm dilute hydrochloric acid, and confirming it by means of mercuric chloride.*

A sixth method depends upon:

1st. The removal of the arsenic from a precipitate of the three sulphides by hydrogen ammonium carbonate.
2nd. The precipitation of the antimony from a solution of the two chlorides by means of pure iron wire, the antimony being separated in the metallic state. The tin remains in solution as dichloride.

* See also Table II.

CHAPTER VI.

REACTIONS OF THE METALS IN GROUP I.

This group comprises the metals silver and lead and mercury in the form of mercurous compounds, which are precipitated from solutions by dilute hydrochloric acid.

1. **SILVER,** Ag′.—This metal occurs native; also as sulphide in silver glance, SAg_2, and in combination with antimony, as sulpho salt in Ag_3AsS_3, dark red silver ore (pyrargyrite), Ag_3SbS_3; with arsenic as silver sulpharsenite, in proustite, Ag_3AsS_3; as chloride, AgCl, in horn silver and other ores.

The colour of metallic silver is white, with a decided red tint, as seen by repeated reflexions from the surface. Its atomic weight = 107·67. Specific gravity, 10·53, and it melts at about 954° C.

It is slightly volatile in a stream of air when very highly heated, and dissolves oxygen when melted, which it gives up again on solidifying. Air and water have no action, but ozone slightly oxidises it. Nitric and sulphuric acids dissolve silver, the latter only when heated. Hydrochloric has only a superficial action. Sulphur combines with the metal directly. SH_2 and other sulphides also give up their sulphur to it. Its salts with the halogens are very sensitive to light, becoming reduced more or less to lower states of combination.

Some of the salts of silver are reduced by free hydrogen being passed through their solutions. All are reduced to metal under the action of nascent hydrogen.

EXPERIMENTS.

I. Silver wire and thin sheet melts easily in a glass tube and leaves a yellow stain on the glass. Otherwise no change.

II. Heated with sulphur the two combine quite energetically, a grey-black crystalline sulphide, Ag_2S, forming, which melts easily, is soft and marks paper. The metal generally glows at the moment of combination.

III. HCl has only a slight surface action scarcely noticeable.

H_2SO_4 when strong and hot dissolves it, slowly forming Ag_2SO_4 and evolving SO_2. $2Ag + 2H_2SO_4 = Ag_2SO_4 + 2H_2O + SO_2$. The sulphate is not very soluble in water and easily crystallises. It bears a high temperature without decomposition.

HNO_3, even when rather dilute, dissolves the metal easily; very strong acid not so rapidly. Oxides of nitrogen are liberated and $AgNO_3$ formed which easily crystallises.

Alkalies have no action, but ammonia dissolves the oxide and many, if not all, its salts.

DRY REACTIONS.

Place a small quantity of powdered silver glance, or the sulphide made in Experiment II., towards the middle of a hard glass tube (combustion tubing of about ¼ inch internal diameter, cut with a sharp file into lengths of 5 to 6 inches answers best). The bent tube used for Experiment I. will do perfectly. Heat the powder gradually by moving the tube about in a Bunsen gas flame, and lastly, heat it strongly towards the centre. By holding the tube in a slightly slanting position, a current of air is made to pass over the ignited sulphide; the sulphur becomes oxidised and is carried off as sulphurous anhydride, readily recognisable by its pungent odour. Metallic silver is left, together with a little silver sulphate.

Other volatile bodies, such as antimony, arsenic (selenium and tellurium), which are frequently present in pyritical silver ores, are likewise oxidised, but are, to a great extent, deposited as As_2O_3 and Sb_2O_3 in the cool part of the tube.

Mix a little of the finely powdered silver glance (or of the roasted ore) with sodium carbonate, and heat upon charcoal under the reducing flame of the blowpipe. A globule of bright metallic silver is left.

Silver ores which contain no other fixed element but silver, are reduced on charcoal to the metallic state by a simple fusion with sodium carbonate. Antimony and arsenic, if present, are readily volatilised as metals before the reducing flame. The sulphur combines with the alkali metal.

Silver ores which contain non-volatile metals, such as copper, iron, &c., as in argentiferous fahl ore, and from which the metal silver could not be eliminated before the blowpipe flame, are treated in the following manner:

About ·100 grm. of the finely-powdered ore is mixed with its own bulk of powdered borax glass; wrapped up in a small piece of assay lead;* introduced into a cavity made in a good piece of charcoal, and fused under the reducing flame of the blowpipe, at first gently, and afterwards more strongly. The heat is kept up till the whole mass has resolved itself into a metallic button and a clear glassy borax bead, which does not adhere to the charcoal. Should the metallic button, on cooling, present a dull grey surface, indicative of the presence of antimony, it is next heated in the oxidising flame, until, on cooling, it shows a bright surface. It is then detached from the borax, cleaned by a blow with a hammer and carefully cupelled on some bone-ash pressed into a shallow cavity in a piece of charcoal, the surface being made smooth and thoroughly concave with the round end of a pestle. The button is thoroughly freed from borax, placed in the cupel, and heated in the oxidising flame. The lead is oxidised and absorbed by the porous bone-ash, forming a mass of fused litharge around the metallic bead. If one cupellation does not yield a brilliant white globule of silver—*i.e.*, if the copper

* Lead free from silver, prepared from lead acetate.

has not been entirely removed—a fact which is indicated by a black colour, instead of a pale yellow colour of the litharge, in the cupel—the cupellation of the button must be repeated in a fresh cupel, and the button, if necessary, remelted with a small quantity of assay lead. The silver not being an oxidisable metal, is obtained in the metallic state.

Small quantities of silver may be separated from lead (as well as from other metals) by cupellation.

Fuse some finely powdered argentiferous galena, PbS,SAg_2, on charcoal before the reducing flame of the blowpipe, either alone or with sodium carbonate. A bead of an alloy of much lead and very little silver is left. Expose this bead on a small cupel (Fig. 16) to the oxidising action of the blowpipe flame. The lead is oxidised and absorbed by the cupel, metallic silver being left.

FIG. 16.

Chloride of silver may be heated on charcoal with sodium carbonate when a bead of metallic silver will be left thus:

$$2AgCl + Na_2CO_3 = 2NaCl + CO_2 + O + Ag_2.*$$

REACTIONS IN SOLUTION.

For the reactions of silver in solution silver nitrate, $AgNO_3$, dissolved in water, is employed.

HCl (group-reagent) and soluble chlorides (NaCl, &c.), give a white curdy precipitate of silver chloride, AgCl, which turns violet on exposure to light. The precipitate is insoluble in water and dilute acids; slightly soluble in concentrated nitric acid; readily soluble in ammonium hydrate, potassium cyanide and sodium thiosulphate; soluble also to a considerable extent in concentrated hydrochloric acid and in strong solutions of alkaline and other chlorides,† more particularly when heated, whence the dissolved silver chloride is, however, reprecipitated on dilution with water.

Collect the precipitated and washed AgCl on a filter and dry in an oven or on a sand-bath. Fuse a portion of the dry salt in a porcelain crucible over a small gas-flame. The white powder fuses; it undergoes a physical change only, and leaves on cooling a hard translucent mass, called horn silver.

Place a small piece of zinc on the fused *horn silver*, and add a drop of dilute hydrochloric acid and a little water. The zinc removes the chlorine and leaves metallic silver. The same action takes place when the white curdy precipitate of silver chloride is brought in contact with strips of metallic zinc.

This forms a convenient method of recovering silver from silver residues.

* The oxygen represented in this equation combines of course with the carbon of the charcoal.

† Silver haloids and cyanide form what are in ignorance termed "double" salts with many other metallic haloid compounds. It is very likely due to a rise in valency of the halogen. Cyanogen can also change its valency.

NaHO or KHO precipitates silver hydrate, AgHO, in the form of a brown powder, which, on ignition, gives off oxygen, and leaves metallic silver.

(NH_4OH), when gradually added, precipitates silver hydrate, readily soluble in excess.

SH_2 precipitates black silver sulphide, SAg_2, from acid solutions; insoluble in dilute acids, in alkalies, alkaline sulphides, and potassium cyanide; readily soluble in dilute boiling nitric acid, with separation of sulphur.

HI or KI gives a yellowish precipitate of silver iodide, AgI, insoluble in dilute nitric acid and almost so in ammonium hydrate (distinction between AgCl and AgI).

HBr or KBr gives a yellowish-white curdy precipitate of silver bromide, AgBr, insoluble in dilute nitric acid; difficultly soluble in ammonium hydrate; readily soluble in potassium cyanide or sodium thiosulphate, or potassium iodide.

HCy or KCy *gives a white curdy precipitate of silver cyanide*, AgCy, soluble in excess of the reagent; insoluble in dilute nitric acid; soluble in ammonium hydrate, but reprecipitated by dilute nitric acid; soluble in sodium thiosulphate. The precipitate is decomposed by concentrated boiling nitric acid; it is decomposed also when heated by itself in a porcelain crucible, to paracyanogen, metallic silver, and cyanogen gas (distinction from AgCl, AgI, and AgBr).

On placing a bright and clean strip of copper into a solution of silver nitrate, the copper becomes rapidly covered with a lustrous coating of metallic silver, and the solution, after a time, gives no precipitate with hydrochloric acid. The silver is deposited on the copper in the metallic state, and the solution contains now $Cu(NO_3)_2$, an eqivalent quantity of copper (63·5 by weight of copper for every 216 of silver) having been dissolved.

Place a small globule of mercury into a concentrated solution of silver nitrate on a watch-glass. The globule of mercury becomes rapidly covered with a crystalline mass, resembling some vegetable growth, termed arborescence. After a time the whole of the silver becomes removed from the solution, and the solution contains mercuric nitrate, $Hg(NO_3)_2$, in the place of the silver nitrate. Metallic silver is precipitated and forms with the mercury an amalgam which is crystalline. This crystalline mass is termed a silver tree (*arbor Dianæ*).

Strips of the metals Zn, Fe, Sn, Pb, Mg and Cd may likewise be employed for the precipitation of metallic silver.

Take a clear solution of one part of grape sugar and 6–8 parts of distilled water, and a somewhat dilute solution of silver nitrate. Heat the latter in a test-tube, nearly to boiling, and add the grape sugar solution. The liquid becomes at once turbid, and a greyish-white powder of metallic silver falls to the bottom; or a yellowish-white metallic deposit forms on the sides of the test-tube, which, on rubbing with a glass rod, shows bright streaks of metallic silver. The metallic silver can be filtered off and fused to a brilliant globule.

The cause of the reduction of the silver salt must evidently be sought for in the grape sugar. It has been seen that silver oxide loses its oxygen readily on ignition. Certain organic substances, such as grape sugar, formic acid, and aldehyde combine eagerly with oxygen. Silver oxide, Ag_2O, which may be supposed to exist in silver nitrate, parts with its oxygen readily to these substances.

This reaction has found an important practical application in the manufacture of mirrors, speculæ for telescopes, &c.

A number of organic substances, mostly acids, can form compounds or salts with silver. These on heating decompose leaving metallic silver, sometimes retaining the shape of the original crystalline substance.

On igniting a few crystals of silver acetate (CH_3CO_2Ag), in a covered porcelain crucible, gently at first, and strongly as soon as no more fumes are given off, a mass of frosted silver is left, having the shape of the original crystals.

2. **LEAD,** Pb''.—Lead is sometimes found native, but more generally in combination with sulphur, as PbS, in galena; also as carbonate, in lead spar or white lead ore, $PbCO_3$; as sulphate, in lead vitriol, $PbSO_4$, in leadhillite, $3PbCO_3,PbSO_4$, and in lanarkite, $PbCO_3,PbSO_4$; as oxychloride, in mendipite, $PbCl_2,2PbO$; as phosphate and oxychloride, in pyromorphite.

The metal has a decided blue colour, and is exceedingly soft; it can be marked by the finger nail, and makes a trail or mark on paper when rubbed over it. It can be obtained in crystals from fusion and slow cooling.

Its atomic weight = 206·4. Specific gravity, 11·37. Melting point, 335° C. Boils between 1450° and 1600° C.

It oxidises superficially only on exposure to air or water, and combines directly with sulphur and the halogens, but not very energetically. Nitric acid dissolves it easily. Acetic acid will also dissolve it if exposed to air at the same time.

EXPERIMENTS.

I. Heated in tube in air Pb. after melting, changes colour, becomes covered with grey ash; on heating further the ash becomes yellow or reddish when hot and paler on cooling. The oxide formed melts easily and attacks the glass, it is PbO.

II. Heated with sulphur, combination takes place, the mass becoming red-hot and melting; it is dull black when cold; brittle; it is PbS.

III. Warmed with hydrochloric acid superficial action takes place, the metal becoming whitened, but little dissolving.

Sulphuric acid when strong also coats the metal with white sulphate ($PbSO_4$), scarcely any dissolving unless the acid be concentrated and boiling when an acid salt is formed.

Nitric acid dissolves it easily, reddish fumes escaping. On evaporating in dish white crystals of lead nitrate ($Pb2NO_3$), are formed. A dilute acid acts quicker than concentrated nitric.

The oxide from I. partly dissolves in HCl, and is converted into white sulphate by H_2SO_4. Nitric dissolves it, forming nitrate.

Soda and ammonia have little effect on the *clean* metal, but soda dissolves oxide of lead to some extent.

Comparatively weak acids, acetic and other organic acids, dissolve lead slowly, especially in contact with air. A white crust of basic or hydrated carbonate forms on the metal.

N.B.—The manufacture of white lead depends upon this behaviour of lead towards organic acids.

DRY REACTIONS.

The principal blowpipe reaction consists in reducing lead compounds on charcoal to metallic lead, either by themselves, or by the aid of sodium carbonate, or potassium cyanide, and in the yellow incrustation of oxide which they yield, which disappears when heated in the oxidising flame, imparting a blue colour to the flame. The compounds of sulphur, antimony, arsenic, and selenium, with lead, are somewhat more difficult to reduce than oxysalts of the metal. The change which takes place when galena is heated with sodium carbonate in a crucible, out of contact with air, is expressed by the equation:

$$7PbS + 4Na_2CO_3 = 4Pb + 3PbSNa_2S + Na_2SO_4 + 4CO_2;\ *$$

but when heated in contact with air, or in the presence of an oxidising agent, such as saltpetre, the loss of lead in the slag is avoided, thus:

$$PbS,Na_2S + 7O + Na_2CO_3 = Pb + 2Na_2SO_4 + CO_2.$$

When galena is roasted in a glass tube open at both ends, it is converted into $PbSO_4$, Pb and SO_2, thus:

(1) $PbS + 2O_2 = PbSO_4$.
(2) $PbS + O_3 = PbO + SO_2$.
(3) $PbS + 2PbO = 3Pb + SO_2$.

With antimonides or arsenides the action is more complex.

With borax and microcosmic salt, lead compounds give in the outer flame a clear yellowish glass when hot which is colourless when cold.†

The presence of antimony, arsenic, and sulphur is indicated when these ores are heated on charcoal by the garlic odour and fumes of As_2O_3, or Sb_2O_3; or in a glass tube open at both ends, white sublimate, fumes, and odour of SO_2.

* This double sulphide when heated with iron filings can be reduced to metallic lead, the iron becoming FeS.

† All lead minerals, especially the antimonial sulpho-salts, boulangerite, bournonite, jamesonite, and argentiferous galena, contain more or less silver, as may be ascertained by carefully cupelling the metallic button on charcoal. (*Comp.* SILVER.)

REACTIONS IN SOLUTION.

For the reactions of lead in solution, the nitrate, $Pb(NO_3)_2$, or acetate $(CH_3COO)_2Pb$ is used, most other lead salts being too insoluble in water.

HCl (group-reagent), or soluble chlorides give, with a not too dilute solution of lead salts, a heavy white precipitate of lead chloride, $PbCl_2$, soluble in much cold water, readily in boiling water, from which the lead chloride crystallises out, on cooling, in fine needles: less soluble in solutions containing dilute hydrochloric or nitric acid. Ammonia converts it into a basic salt, of the composition PbHOCl (lead chlorohydrate)—a white powder almost insoluble in water.

NaHO or KHO precipitates lead hydrate, $Pb(HO)_2$, soluble in excess of the reagent, especially on heating. The $Pb(HO)_2$ must be viewed as acting the part of a weak acid, compared to the alkaline bases KHO and NaHO, or the compound may be looked upon as a substituted hydrate, thus:

$$Pb\genfrac{}{}{0pt}{}{OH}{OH} + KHO = Pb\genfrac{}{}{0pt}{}{OK}{OH} + H_2O.*$$

NH_4OH precipitates a white basic salt, insoluble in excess. The precipitate forms only slowly in a solution of lead acetate.

SH_2 precipitates black lead sulphide, PbS, from acid solutions. If a large excess of hydrochloric acid be present the precipitate is reddish-brown, consisting of Pb_2SCl_2 (lead sulphodichloride). On diluting considerably with water, a black precipitate is obtained.

$(NH_4)_2S$, or soluble sulphides, precipitate black PbS, insoluble in dilute acids, alkalies, and alkaline sulphides. Lead sulphide is soluble in hot dilute nitric acid, lead nitrate being formed, with separation of sulphur. Concentrated nitric acid converts it into $PbSO_4$; the oxidation extending to the sulphur as well.

H_2SO_4, and soluble sulphates, precipitate a white sulphate, $PbSO_4$, almost insoluble in water, especially in the presence of excess of dilute sulphuric acid; insoluble also in cold dilute acids, soluble in boiling hydrochloric acid, from which lead chloride crystallises out on cooling; soluble in potassium hydrate, and readily soluble in concentrated solutions of certain salts, such as sodium thiosulphate, ammonium acetate or tartrate, in the presence of excess, of ammonium hydrate, from which solutions H_2SO_4, in excess, $(NH_4)_2S$, or potassium chromate, precipitate the lead again. Boiling with sodium carbonate converts $PbSO_4$ into an insoluble basic carbonate. Lead sulphate separates from very dilute aqueous solutions very slowly or only on the addition of alcohol (methylated spirit).

Potassium chromate precipitates yellow lead chromate, $PbCrO_4$

* This kind of combination may also exist in the case of $Zn(HO)_2$, $Al_2(HO)_6$, and others which dissolve in solutions of alkaline hydrates. Hydrates are relatively either positive or negative.

(chrome yellow), readily soluble in potassium or sodium hydrates, difficultly soluble in dilute nitric acid, insoluble in acetic acid.

Soluble carbonates give a white precipitate of a basic carbonate (a sort of white lead), of varying composition, usually represented as $2PbCO_3$, $Pb(OH)_2$, insoluble in water and in potassium cyanide.

KI gives a yellow precipitate of iodide, PbI_2, soluble in excess of the reagent; also soluble in much hot water, from which it separates on cooling in beautiful golden-yellow scales. The water solution is colourless.

KCy precipitates white cyanide, $PbCy_2$, insoluble in excess, soluble in dilute nitric acid.

Soluble phosphates, arsenites, and arsenates, silicates, borates, oxalates, tartrates, citrates, ferro- and ferricyanides give precipitates with lead salts, which are insoluble in water, but soluble in dilute, or strong, nitric acid. These precipitates possess, however, only a secondary interest from an analytical point of view.

Metallic iron or zinc precipitates lead from its salts. This is seen very strikingly on dissolving a few ounces (30 or 40 grms.) of lead acetate (sugar of lead) in distilled water, with the addition of a little acetic acid, and suspending in the solution a piece of zinc from a thread. The zinc becomes covered with a beautiful crystalline deposit of metallic lead, which increases rapidly if the solution be left undisturbed, and acquires the appearance of the branch of a tree (*arbor Saturni*). The metallic structure can be preserved for days in unaltered beauty. On removing the precipitated lead from the piece of zinc, the latter is found much corroded and considerably diminished in size and weight. The lead may be collected on a filter and washed with water, dried, and fused in a crucible, under a covering of borax, to a bright metallic button. A chemically equivalent mass of zinc to the precipitated lead (*i.e.*, 65 parts by weight of zinc for every 207 of lead) has dissolved, and is found in the solution, in the form of zinc acetate. The atomic weights of Zn (65) and Pb (207) can be determined roughly, by weighing the metallic zinc, before and after immersion, as well as the precipitated lead.

Heat a little red lead, Pb_3O_4,* in a small porcelain crucible, or in a test-tube, to which a delivery-tube is attached. Oxygen gas is given off, which may be collected in the usual manner over water. The residue is dark yellow, and on cooling turns bright yellow. It consists of lead oxide, PbO (litharge) according to the equation:

$$2Pb_3O_4 = 6PbO + O_2.$$

Treat a little Pb_3O_4 with strong hydrochloric acid in a test-tube, and heat gently. A greenish-yellow gas comes off, and lead chloride is produced in the solution. The gas is readily recognised as chlorine by its property of bleaching litmus-paper:

$$Pb_3O_4 + 8HCl = 3PbCl_2 + 4OH_2 + Cl_2.$$

* The composition of commercial red lead is more correctly expressed by the formula Pb_4O_5.

Treat another portion of red lead with dilute nitric acid. The red colour changes to brown—the colour of lead dioxide, PbO_2. The reaction is expressed by the equation:

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2OH_2.$$

Lead can thus combine either with one or two atoms of oxygen to form PbO or PbO_2; and red lead may be regarded as a compound of these two oxides.

The minerals plattnerite, PbO_2, and minium, Pb_3O_4, represent the corresponding natural oxides.

H_2SO_4 forms with PbO the sulphate, $PbSO_4$, oxygen being given off.

PbO_2 absorbs sulphurous anhydride readily, forming $PbSO_4$.

HCl on heating with plumbic dioxide yields chlorine.

3. **MERCURY.**—(Mercurosum) $'H'_2$. (See *ante*).

A solution of mercurous nitrate, $Hg_2(NO_3)_2$, is used, most of the other mercurous salts being insoluble.

HCl (group-agent), or soluble chlorides, give a white precipitate of mercurous chloride, Hg_2Cl_2 (calomel), which is insoluble in dilute acids and is blackened by KHO or NH_4OH; the latter converts it into mercurosoammonic chloride, NH_2Hg_2Cl. Mercurous is converted into mercuric chloride by the action of chlorine water. Concentrated hydrochloric acid converts it, upon long-continued boiling, into $HgCl_2$ and grey metallic mercury. Nitric acid oxidises it readily into $HgCl_2$ and $Hg(NO_3)_2$, with evolution of nitrous fumes. Dry Hg_2Cl_2 sublimes unchanged.

NaHO or KHO gives a black precipitate of mercurous oxide, Hg_2O, insoluble in excess.

NH_4OH produces a black precipitate of basic dimercurosoammonium nitrate, $(NH_2HgNO_3)_2Hg_2O$.

The precipitate is insoluble in excess.

SH_2 precipitates black mercurous sulphide, $'Hg'_2S$,* insoluble in excess or in dilute acids; soluble in aqua regia or in yellow potassium sulphide. When boiled with concentrated nitric acid, the second atom of mercury in Hg_2S is converted into $Hg(NO_3)_2$, and a white compound of mercuric nitrate and sulphide is formed.

$(NH_4)_2S$ produces the same black precipitate.

A clean strip of metallic copper precipitates metallic mercury from mercurous solutions, cupric nitrate being left in solution. On gently rubbing the greyish deposit with a piece of wash-leather, the surface becomes bright and shining like silver. The more electropositive metals, Bi, Cd, Cu, Fe, Pb, Zn, precipitate the less electropositive metal Hg.

Sulphurous acid, ferrous sulphate or stannous chloride produce a grey precipitate of metallic mercury. On decanting the liquid and

* This compound appears to be a mixture of mercuric sulphide and mercury, as is shown by the ready action which concentrated nitric acid has upon it.

boiling the grey deposit with hydrochloric acid, distinct metallic globules are obtained. The changes may be expressed thus:

$$Hg_2(NO_3)_2 + H_2SO_3 + OH_2 = 2Hg + 2HNO_3 + H_2SO_4.$$
$$3Hg_2(NO_3)_2 + 6FeSO_4 = 6Hg + 2Fe_2(SO_4)_3 + Fe_2(NO_3)_6.$$
$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = 2Hg + SnCl_4 + 2HNO_3.$$

Mercurous salts thus act the part of oxidising agents, when coming in contact with more powerful reducing agents.

A method of separating the metals of Group I. will readily suggest itself from the following facts:

1st. The solubility of $PbCl_2$ in boiling water.
2nd. The solubility of AgCl in NH_4OH.
3rd. The conversion of the Hg_2Cl_2 into black NH_2Hg_2Cl by the action of NH_4OH.

Table I. in the analytical Tables embodies this method of separation, but this is not the only method available.

Before proceeding to the study of the reactions for acids, the student will do well to tabulate in a concise way the knowledge gained of all the metallic oxides and hydrates, sulphides, carbonates, neutral as well as basic, &c., and to commit the reactions to memory, if possible, or at any rate make use of them so as to evolve other methods of separation therefrom.

He will also gain much precise information by working out in a tabular form illustrated by equations:

(1) The solubility of all the metals hitherto treated of—

(*a*) In dilute and concentrated hydrochloric acid.
(*b*) In dilute and concentrated nitric acid.
(*c*) In dilute and concentrated sulphuric acid.
(*d*) In aqua regia.

(2) The solubility of the metallic oxides and sulphides obtained by double decomposition in solution, in the different acids, in caustic alkalies, and in alkaline sulphides.

CHAPTER VII.

NON-METALLIC ELEMENTS.

THE non-metals are more varied in physical character than the metals; some are solids but lack any general property, like metallic lustre. One at least is liquid and five are gases at common temperatures. They are as a rule bad conductors of heat and electricity, but to this there are exceptions. There is a peculiarity very evident amongst non-metals which is not yet much known amongst metals in that some of them under certain conditions can exist in very different physical states, and this difference in physical state is to some extent attended by a considerable difference in their chemical behaviour. They are said to form allotropic varieties.

CARBON, C'', ^{iv}. Varieties: α, diamond; β, graphite; γ, charcoal. Atomic weight, 11·97. Vapour density undetermined; not volatile at any known temperature. Specific gravity diamond, 3·52; graphite 2·17; charcoal various, depending on source, from 1·1 to 1·5.—Diamond is the hardest body known. Wood-charcoal is friable and marks paper with a dull black streak. Graphite makes a shiny and not quite black mark. Cokes, from coal, and gas carbon do not mark paper. Melting point of carbon unknown, fusible and volatilised in the electric furnace only. Carbon occurs in nature in two distinct crystalline modifications as diamond and graphite. The several modifications exhibit great diversities of colour, lustre, transparency, hardness, and power of conducting heat and electricity. With the exception probably of melted iron, C is insoluble in all known solvents.*

γ-Carbon when subjected to a red heat burns in the air or oxygen with production of carbonic anhydride; the more compact forms of carbon, graphite, or gas carbon burn with difficulty in the air alone. α-C, or diamond, will not burn even at a red heat in air, but readily

* Under the conditions of the "electric furnace" carbon combines with metals forming a class of compounds termed "carbides." The chemistry of these compounds is not by any means fully worked out. Some of these carbides are easily decomposed by water and acids or alkalies, and some hydrocarbons appear as constant products of these decompositions. Calcium carbide, probably CaC_2, has rapidly became a commercial article and is the best known example of the class. By the action of water it gives acetylene, C_2H_2, as the main gaseous product:

$$CaC_2 + H_2O = CaO + C_2H_2.$$

Some of the other carbides, as manganese, give hydrocarbons with more hydrogen, as CH_4 or C_2H_6, &c.

in pure oxygen. Graphite or diamond is not attacked by strong nitric acid, but charcoal is oxidised. On boiling charcoal with sulphuric acid the acid is decomposed, with the production of carbonic and sulphurous anhydrides and water:

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2OH_2.$$

Charcoal is also oxidised by a mixture of hydrochloric acid and chlorate of potash. A mixture of nitric acid and potassium chlorate attacks graphite on long boiling. The lighter forms of carbon are also oxidised by chromic acid, in the presence of sulphuric or nitric acids. The best test for carbon is the production of CO_2 by combustion in air or oxygen. Carbon exists in the free and combined state in iron and steel, also in certain minerals; in the latter case its detection is not easy in the presence of carbonates.

Carbon does not combine directly with clorine, bromine, or iodine at any temperature, but does with fluorine even at very low temperatures, and the γ-modification combines readily with sulphur and selenium at a low red heat. There is just a doubt whether diamond is carbon only.*

EXPERIMENTS.

I. Carbon is unaltered by air or water at ordinary temperatures.

Moderately pure charcoal can be made by heating some clean cotton wool or cellulose on a retort to redness and until no more gases are given off.

This charcoal retains the shape of the original cotton because the cellulose decomposes before melting.

Sugar heated in a retort melts, gives off gases, and a quantity of carbon will be finally left, but it has no particular shape owing to the sugar having melted. This charcoal is denser and harder than that from cellulose.

The charcoal from different sorts of wood differs a good deal in hardness, gravity and purity as far as mineral substances are concerned.

Animal charcoal made from bones contains very much mineral matter, calcium salts, &c. Coke is charcoal from coal. It is best made by heating coal in a covered platinum crucible until gases cease to be evolved.

II. Heated in tube in air, charcoals and coke fire at a red heat and glow, but there is no flame if pure; *Graphite, gas-carbon and diamond only burn in oxygen gas when heated to bright redness in it.*

The product in all cases is CO_2. On moistening a test tube with lime water and inverting it over the end of the bent tube whilst the substance is being heated a white deposit will form on the sides of the tube.

Baryta water, or if that fails, a solution of a lime or baryta salt made alkaline with ammonia may be used.

III. Acids.—Hydrochloric has no action under any circumstances. Strong sulphuric boiled with charcoal or coke is decomposed, SO_2 and CO_2 being formed. No other carbon is affected.

Strong nitric oxidises and sometimes ignites charcoal, but it is practically without action on other carbons. Chromic acid, CrO_3, also oxidises charcoals and coke, especially when assisted by sulphuric acid.

IV. All the forms of carbon are more or less rapidly affected by nitre when ignited with it in a platinum cup; potassium carbonate is formed.

V. Solutions of alkalies have no action, but melted KHO attacks charcoals and coke at a red heat.

* Diamonds are said to be formed when carbon is dissolved in iron at the "arc" temperature and the "melt" then suddenly cooled.

SILICON, Si^{iv}. Varieties: *a*, adamantine; *β*, graphitic; *γ*, amorphous. Atomic weight, 28. Specific gravity, *a* = 2·19 to 2·49. *β* (graphitic) = 2·00.—This element, although widely distributed in nature, is never found in the free state, but chiefly in combination with oxygen, in the crystalline condition as quartz, &c., and in the amorphous condition as opal, flint, &c.

Silicon is found in cast iron in a condition perhaps analogous to the state in which carbon exists.

It is supposed to melt between the melting point of cast iron and steel, but this is doubtful.

Amorphous silicon is a dark brown powder which soils the fingers. When heated in the air it takes fire, burning to SiO_2. Heated in a vacuum it becomes denser and assumes a graphitic appearance, after which it oxidises much less rapidly on heating.

It may be easily obtained by heating sand, SiO_2, with magnesium filings, and after cooling, washing the product with very dilute HCl.

Hydrofluoric is the only acid which singly attacks silicon.

Heated with caustic potash or soda silicates are formed with evolution of hydrogen:

$$Si + 4KHO = Si(KO)_4 + 2H_2.$$

Many metals when in a fused state dissolve and perhaps combine with silicon—for instance, iron, aluminium, magnesium, and others. On cooling, the Si crystallises out to some extent, and may be isolated by treating the metal with an acid, as dilute HCl.

Some silicon bronzes are used to a limited extent.

It combines directly with the halogens and also with sulphur at a high temperature. From the haloid compounds direct carbon compounds have been formed, so-called organo-silicon compounds. From these haloid compounds Si is obtainable by the action of the alkali metals.

EXPERIMENTS.

I. Silica in the form of sand, flint or rock-crystal is the most abundant silicon compound.

It is SiO_2 and undergoes no change when heated. Acids and most other reagents have little or no action.

II. Fine sand mixed with magnesium powder or filings and heated in a tube is reduced to silicon and a compound of magnesium and silicon, $SiMg_2$. The mixture gets very hot during the reaction and often flies out of the tube. 1 grm. fine sand and ·25 grm. Mg filings will be enough at once. On putting the product into dilute HCl, hydrogen and SiH_4 are given off, and the SiH_4 generally takes fire. A brown powder settles down which should be washed once with very dilute HCl and then with alcohol and dried.

The brown amorphous Si may be (i) heated in a tube in air—it should glow; (ii) heated with NaOH—hydrogen is evolved.

BORON, $B^{\prime, iii}$, *a*, *β*, *γ*. Atomic weight, 10·94. Specific gravity, 2·53.—Boron occurs in nature in borax and boracic acid; never in the free state. Three varieties of boron are known, amorphous, *γ*; mono-

clinic, β; quadratic, α; the latter variety is nearly as hard as the diamond itself. Some of these varieties have been obtained by dissolving boron in melted metals; for instance, aluminium, and there is some doubt whether all the solvent metal has been quite removed. Amorphous boron when unignited is slightly soluble in water, but not in water containing acids or salts.

Amorphous boron is a brown powder which does not oxidise in the air or in oxygen gas at ordinary temperatures, but at about 300° C. it burns, the product being boric oxide or anhydride, B_2O_3.

Boron unites with nitrogen, the halogens, and sulphur directly, and also with some metals. It forms three classes of compounds, direct binary compounds of boron and another element and two oxidation stages.

This element is not used as such, but its compounds with oxygen are largely employed.

EXPERIMENTS.

The oxide B_2O_3 is the most common oxygen compound; it is contained in *borax which is much employed as a flux for soldering.*

I. Heated in tube B_2O_3 simply melts, but no further change takes place.

It dissolves in water, acids and alkalies, but without any characteristic reactions.

The solution in water is very faintly acid, if at all. Turmeric paper turns brown as it does with an alkali. It distils rapidly with steam and can thus be evaporated away.

II. The acid is obtained by making a strong solution of borax, $B_4O_7Na_2$, in water and adding HCl. White crystals quickly form. If the water be poured away and alcohol added to the crystals they dissolve. The alcohol solution, warmed in a test tube and the alcohol vapour set alight, burns with a green-edged flame. This distinguishes boron, or boric acid, from copper or barium, neither of which are carried up in alcohol vapour.

III. Amorphous boron may be obtained in a similar way to silicon by heating a mixture of dry borax or B_2O_3 with magnesium filings in a strong tube. The action is energetic. After cooling the product is to be treated with very dilute HCl once or twice, and then washed with alcohol. It is a *brown powder after drying.*

IV. Heated in air in the open tube it burns, forming B_2O_3. It should be heated with sulphur and alkalies and acids and results noted.

OXYGEN, O'', α and β. Atomic weight, 15·96; liquid under ordinary pressure at -193°. Specific gravity, α liquid, 0·979–0·989; as gas, 1·105 (air = 1); 1 litre = 1·429 grm. Oxygen occurs in nature, in the free state in the atmosphere and in immense quantity combined with metals, as oxides, silicates, carbonates, &c. Although the absolute amount of free oxygen contained in the air is very great, the proportion which the free oxygen bears to that in a state of combination is but very small.

α-Oxygen dissolves appreciably in water; some metals also absorb oxygen when in the molten state, and give it off again on cooling—*e.g.*, silver. From the energy of its chemical combinations with other substances, oxygen is very easy to distinguish. It forms compounds with nearly every other elementary body, in many cases directly.

All bodies that burn in air burn in oxygen with increased brilliancy, such as phosphorus, carbon, sulphur, &c.

Free oxygen is absorbed by pyrogallic acid rendered slightly alkaline by potash or soda, and this test is used in gas analysis. The solution rapidly turns brown when much oxygen is present.*

The other modification of oxygen, ozone, or β-O, also occurs in air, especially in country districts and over the sea. It can also be prepared by passing the silent electrical discharge through pure oxygen, when a portion of the gas will be converted into ozone; by the electrolysis of dilute H_2SO_4 under certain conditions; also when electric sparks pass through air, or when a blowpipe flame is supplied with considerable excess of air, and when some substances are undergoing a partial oxidation. Phosphorus shows this very well. It must be ordinary phosphorus and the air for its oxidation must be moist. The reaction is still somewhat doubtful, but as P_2O_3 is possibly the essential product the action may be:

$$P_2 + {}^3O_2 = P_2O_3 + O_3$$

which means that three molecules of ordinary oxygen are simultaneously broken up.

It must not be imagined that all the oxygen in contact with the phosphorus is so converted. Really only a few per cents. of ozone are formed.

One of the most characteristic tests for ozone is its effect on mercury. The metal at once loses its mobility, and adheres to the surface of the glass in a thin mirror. A single bubble of oxygen containing ozone will alter the appearance of several pounds of mercury, taking away its lustre and the convexity of its surface. Free a-oxygen has no action on potassium iodide, whereas β-O decomposes it into free iodine and potassium hydrate. Potassium iodide and starch paste, or paper smeared over with a mixture of the two, when exposed to β-oxygen, becomes of a purple or deep blue colour, due to the liberated iodine combining with the starch.

Oxygen is most easily obtained from chlorates by heating them. The gas is a little heavier than air (·2), and may be collected by downward displacement of air in a bottle, with care but is most generally collected over water.

* A solution of copper oxide in ammonia, rendered colourless by digestion with excess of metallic copper; otherwise a solution of cuprous oxide in ammonia, absorbs oxygen and turns blue. This is a very delicate test for free oxygen. The reagent is best made by dissolving cupric chloride in strong HCl, and boiling the solution with some copper turnings. It will produce a dark-brown solution, which is thrown into a considerable quantity of water which has previously been boiled to expel air, and then cooled. A white precipitate of Cu_2Cl_2 is formed, which may be washed with dilute alcohol and dried. It will then keep any time. A small quantity is then dissolved in strong ammonia in a small bottle kept quite full and also containing copper turnings. Taking out the stopper in the air will be sufficient to cause a blue coloration. Ferrous oxalate dissolved in an alkaline oxalate also absorbs O rapidly, turning dark red.

EXPERIMENTS.

I. Pound up about 5 grms. potassium chlorate, introducing into a test tube or small flask with cork and delivery tube, heat until the salt melts and boils, collect the gas in several tubes or cylinders, best over water. It is

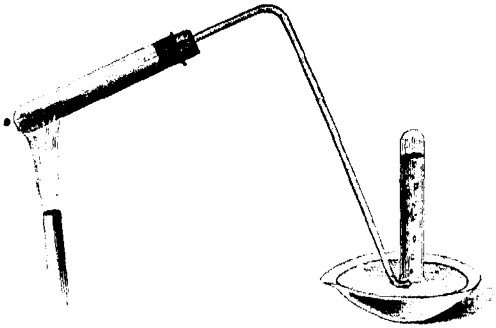


FIG. 17.

much safer to mix a little, about 1 grm., MnO_2 (or a still smaller quantity of $K_2Mn_2O_8$) with the chlorate first. The gas then comes off more regularly and less violently than with a chlorate alone. Should the tube get stopped up by particles of chlorate it becomes a very dangerous experiment. In one tube introduce a piece of charcoal held by a wire, which has been just lighted at one point—it will begin to burn brightly; or a taper, blown out so as to leave only a spark, will re-light, and burn brighter than in air. In another tube of the gas suspend a piece of neutral-tint litmus paper, and a piece of iodised starch paper; neither should be affected if the oxygen be pure.

II. Oxygen is completely absorbed by an alkaline solution of pyrogallol. To prove this, collect about half of a tube of oxygen over, measure, or indicate where the water stands by a strip of paper stuck on, unless the tube is graduated; then introduce a few cubic centimetres of a solution of pyrogallol, to which some soda or potash has been added. This is easily done by means of a bent pipette made from a glass tube.

N.B.—Experiment II. is best done in a tube over mercury. The other absorbents, ferrous exalate, &c., may then be tried.

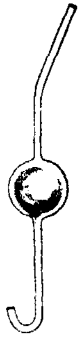


FIG. 18.

SULPHUR, S″, ^iv, ^vi. Several varieties. Atomic weight, 31·98. Specific gravity, α (rhombic) = 2·07; β (monoclinic) = 1·96; γ (amorphous) = 1·92. Melting point depends on variety, ranging between 112° C. and 120° C.; solidifies, 114° C. Boiling point, 440° C. Is found in nature in the free or native state in the neighbourhood of extinct, as well as active volcanoes, in Sicily, and many other places.

It occurs in commerce either in sticks, known as roll sulphur, or

in the amorphous state as a pale yellow powder, known as flowers or flour of sulphur.

It is a very bad conductor of heat and a non-conductor of electricity. Is exceedingly brittle under a sharp blow and cracks in all directions when a piece is rapidly heated.

Sulphur inflames, when heated just to vaporising, with a bluish flame, producing sulphur dioxide gas, SO_2, which has a pungent odour. It is not attacked by dilute or concentrated HCl, but decomposes concentrated sulphuric acid on heating, with evolution of SO_2, and formation of water:

$$S + 2H_2SO_4 = 3SO_2 + 2OH_2.$$

It is oxidised slowly by fuming nitric acid, more readily under pressure, also by hydrochloric acid and potassium chlorate, and by aqua regia, with formation of sulphuric acid. Permanganate also oxidises it slowly.

It is dissolved freely by carbon disulphide, less readily by oil of turpentine, both of which deposit crystals of sulphur on evaporation.

Caustic alkalies also dissolve sulphur readily with formation of metallic sulphydrate and thiosulphate.

$$4KHO + S_4 = 2KHS + H_2O + K_2S_2O_3.$$

Sulphur vaporises to a slight extent at ordinary temperatures, so that some metals, as Cu, Ag, Hg, Pb, placed in its vicinity become slowly converted into sulphides. The halogens, and most metals, even those that do not oxidise, combine with sulphur directly. It can exist in three, possibly four, states of combination, especially with oxygen, giving rise to various classes of compounds.

Sulphur is best recognised by means of its two well-known oxidation-products, sulphurous and sulphuric oxide, SO_2, SO_3; oxides of the forms S_2O_3 and S_2O_7 also exist, but are very unstable.

EXPERIMENTS.

I. Heated in the tube sulphur melts and becomes much darker in colour; before taking fire it sublimes and forms a pale yellow coating on the upper cool part of tube. A small piece may be entirely evaporated without taking fire in the air current. Heated more quickly it takes fire and burns with very pale blue flame and a faint white smoke escapes. On holding a piece of moistened blue litmus paper over the open end of tube, it becomes red from action of oxide SO_2, at same time odour of gas is perceptible. A test tube moistened inside with lime or baryta water, as with CO_2, becomes clouded or whitened. A piece of filter paper just coloured with a drop of permanganate solution becomes bleached. Bichromate may also be used, it becomes green on contact with the SO_2. CO_2 does neither of these.

II. Melt and boil some sulphur in test tube or flask and pour out in a thin stream, whilst hot into cold water; an elastic mass is produced called plastic sulphur. It may be drawn out into threads, but becomes brittle again in a few hours.

III. Hydrochloric has no action on sulphur. Sulphuric, concentrated,

dissolves it on heating, becoming yellow coloured. If boiled on it SO_2 is formed, but slowly.

Nitric oxidises sulphur slowly when boiled on it. Alkalies, as KHO and NaHO, dissolve it, making a yellow solution. On putting HCl to this solution, some sulphur is precipitated as a white powder.

IV. Turpentine when hot dissolves it easily, and on cooling, crystals of sulphur are obtained. Boil the sulphur in the turpentine in a test tube and pour the solution into a dish to crystallise.

Carbon disulphide, CS_2, dissolves sulphur most easily, without heating. On evaporating in the dish spontaneously by exposure to the air long crystals may be obtained.

V. Dropped into melted KNO_3 sulphur burns with a white flame, the product is K_2SO_4 and nitrogen and sometimes oxides of nitrogen escape.

NITROGEN, $N^{i, iii, v}$. Atomic weight, 14. Specific gravity, 0·963. Specific gravity of liquid at 0° C. and 275 atmospheres pressure = 0·37; liquid under ordinary pressure at −193°–200°. 1 litre weighs 1·245 grm.—Nitrogen exists in the air in the free state mechanically mixed with oxygen; and combined in certain salts, as nitrates, and in both vegetable and especially animal substances.

Nitrogen does not combine with ordinary combustibles, as charcoal or a taper, nor is it combustible itself under ordinary conditions. But when a powerful induction spark passes through a mixture of nitrogen and oxygen (air) a decided combination takes place, and if the spark be a moderately large one the appearance of a flame, which can be blown about, is produced between the terminals of the coil. Oxides of nitrogen are the result. With some few elements it combines quite energetically, for instance, titanium, boron, magnesium, and with others, but less easily. Otherwise it is somewhat inert, being neither acid nor alkaline and not affecting any liquid reagent. Most of its compounds are "endothermic," some of them to a considerable extent, relatively, and are in consequence more or less explosive.

It is difficult to obtain pure nitrogen from air, although present in such a large proportion (80 per cent.), on account of the argon also present.

It may be obtained pure from nitrites and ammonia salts by the reaction:

$$KNO_2 + NH_4Cl = KCl + 2H_2O + N_2.$$

EXPERIMENTS.

I. About five grams potassium nitrite and four of ammonium chloride will give sufficient nitrogen to examine its properties. They are dissolved in water, not too much, in a small flask or large test tube fitted with cork and tube, and on warming gently the action commences and the gas may be collected in a few tubes over water.

II. Suspend in a tube of the gas moistened litmus, blue and red, they should not change.

III. A lighted match is extinguished on being put in the gas.

IV. The gas is not absorbed by potash or any other reagent.

V. A glass rod dipped in lime water and held in the gas is not altered.

VI. Some of this nitrogen should be tested as follows to see the combina-

tion with magnesium. A tube is arranged somewhat as in Fig. 19. Nitrogen is driven through for some time to expel air and then the stopper closed. On now heating the Mg to redness absorption will take place and the mercury rise in the long tube, showing that almost a vacuum is produced.

The magnesium nitride produced is red whilst hot, and very pale yellow when cold. On placing in water the nitride decomposes, giving off ammonia :

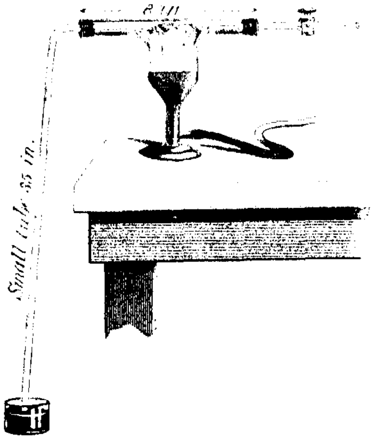


FIG. 19.

$$Mg_3N_2 + 3H_2O = 3MgO + 2NH_3.$$

Mg ribbon burnt in air combines also with some N, and on putting the white ash in water a little ammonia is formed.

PHOSPHORUS, P', ''', v, α, β, γ. Atomic weight, 30·96. Vapour density, 4·35 to 4·50. Specific gravity, ordinary waxy, α, 1·76—1·83. Red β, 2·20; metalline γ, 2·34. Melting point, 44°.—Phosphorus never occurs in nature in the free state, but chiefly in combination with lime and alumina as phosphates.* It comes in commerce in two forms—viz., common colourless or octohedral phosphorus, usually in the form of sticks, and the red or amorphous phosphorus in the form of powder.

Ordinary phosphorus is nearly insoluble in water, readily soluble in chloride of sulphur and carbon disulphide, from which crystals of phosphorus can be obtained on evaporation, and in most organic liquids as ether, alcohol, benzene, vegetable and mineral oils, &c. &c. The luminosity of free phosphorus in the dark, and the peculiar smell of this element produced when it is exposed to air and slowly oxidising, renders its detection comparatively easy. Phosphorus is a bad conductor of electricity either in the fluid or solid state. It is highly poisonous.

Ordinary, or α-phosphorus, is extremely inflammable, taking fire in the open air, often spontaneously; it burns with a yellowish-green flame, emitting dense white fumes of phosphoric anhydride and some lower oxides.

It is not attacked by strong hydrochloric acid except under pressure, but concentrated sulphuric acid is reduced by it to sulphurous anhydride, and on heating even to sulphur.

Nitric acid oxidises it to phosphoric acid on long-continued boiling.

Very minute traces of free phosphorus may be detected by the characteristic flame like that of phosphoretted hydrogen, which is evolved when the substance containing it is exposed to the action of

* See Calcium and Alumina for minerals.

nascent hydrogen. The substance is introduced into a flask fitted up like Marsh's apparatus for the detection of arsenic. If phosphorus be present, the evolved gas contains phosphoretted hydrogen, and will burn with a green flame when the end of the jet is kept cool. The burnt gases may also be aspirated through a nitric acid solution of ammonium molybdate, when a characteristic yellow precipitate will be formed, or through a solution of $AuCl_3$, when an intense red colour will be produced by the reduction of metallic gold in a fine state of division. A piece of blotting-paper, moistened with silver nitrate, and held in the gas, will become brown or black when only most minute traces of phosphorus are present. Sulphides must, of course, be absent.

Red, or β-phosphorus, is obtained by heating α-phosphorus to between 300° and 400° out of contact with air. It is insoluble in all solvents, and not acted upon by oxygen at the ordinary temperature. It burns like α-phosphorus, however, when heated in the air to about 300° C. Chlorine or iodine combine with it directly, and if water be present both hypophosphorus acid, HPO_2, phosphoric acid and a haloid acid are produced.

The phosphoric acid may then be tested for by a nitric acid solution of molybdate. A very small particle of β-phosphorus, a bit of safety-match box striker, will give the reactions of phosphorus on warming with a small crystal of iodine and one drop of water in a test-tube, and after the reaction a few drops of nitric acid and ammonium molybdate added. Phosphorus is contained in some alloys known as phosphor bronzes.

EXPERIMENTS.

Waxy phosphorus is sold in sticks or rods and kept under water; they have generally a whitish coating, supposed to be produced by the action of light. Amorphous, or red phosphorus, is a powder of more or less purple-red colour.

Very great care must be taken in handling waxy phosphorus as it is liable to take fire in air and the burn is difficult to heal. It must be cut whilst wet with water and dried by a little blotting paper. For the experiments a very small piece, not larger than an ordinary match head may be taken. The same amount will also be enough of the *red phosphorus.*

I. Heated in a tube *ordinary P.* melts on very gently warming and gives off a peculiar odour. It very quickly takes fire and gives a thick white smoke; a piece of blue litmus paper held in this smoke, as it escapes from the upper end of tube, is reddened. The tube will have yellowish or red rings left in it above where the piece of P. was. These are due to some of the red or β-P. formed by some phosphorus vapour being heated to the "changing" temperature. β-phosphorus requires to be much more strongly heated before it takes fire. The same products are formed as it burns.

II. A tiny piece of waxy P. dropped into about half an inch of turpentine or sulphide of carbon in a test tube dissolves almost immediately on contact. On allowing the solution to evaporate in a dish or pouring a few drops on blotting paper it takes fire spontaneously when the solvent has evaporated.

III. Sulphuric when concentrated and boiled on phosphorus oxidises it, SO_2, and sometimes even sulphur being liberated. Strong nitric oxidises and dissolves both kinds of P. the waxy quicker. Red fumes of oxides of nitrogen are evolved and phosphoric acid formed. On evaporating the nitric away a

clear glassy substance, metaphosphoric acid, is left. Hydrochloric acid has no action on either kind of phosphorus.

IV. A small piece of dry α-phosphorus, very gently warmed in a test tube with a tiny crystal of iodine, rapidly undergoes the change into the β modification. At the same time some phosphorus iodide, PI_2, is formed. If any moisture be present this decomposes and fumes of HI escape from the tube.

V. Alkalies, including CaO and BaO, but not ammonia, when warmed with α-phosphorus give off PH_3 and a salt of H_3PO_2 is formed. This should be done in a test tube only. It may have a cork and delivery tube.

$$3Ba(OH)_2 + 2P_4 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3.$$

VI. Phosphorus, either α or β, combines directly with metals. Place a small particle of β-P. on a piece of platinum foil—heat over the flame. At about the temperature of changing a phosphide of platinum forms and melts a hole.

The Halogens.—The four substances, F, Cl, Br, I, form a very well marked group of elements. This is shown both by their physical and chemical properties.

Boiling points of the halogens in absolute degrees:

F	87°	=	−196°
Cl	240°	=	−33°
Br	337°		+64°
I	460°		+187°

FLUORINE, F. Atomic weight, 19.—Fluorine occurs in combination with calcium, aluminium, potassium, sodium, &c., in minerals like fluor spar, cryolite. It is also found in the teeth and bones, and in many silicates and phosphates, and hence occurs in soils in small quantities, from whence it is taken up by plants. The hydrogen compound of fluorine is treated of under "Acids."

Fluorine is a gas, under ordinary conditions of temperature, which attacks nearly all substances, metals or non-metals, and many compounds, especially if they contain hydrogen. With oxygen and nitrogen it does not seem to combine.

The most satisfactory method of preparation (isolation) is by the electrolysis of KF in solution in anhydrous HF, at a low temperature in a platinum vessel. Glass vessels cannot be employed at any temperature much above that of boiling oxygen (−183°) on account of the formation of SiF_4 which seems almost as strong a tendency as that towards hydrogen. On cooling to about −187° fluorine forms a pale yellow liquid of great mobility. At this low temperature nearly all its chemical activity ceases, for silicon, boron, carbon, sulphur, phosphorus, and some other elements are not affected, nor are iodides decomposed, but benzene and turpentine become incandescent and with hydrogen it explodes.*

Liquid fluorine seems to mix in all proportions with liquid air. It does not solidify at −210°. Its density is 1·14; its capillarity is less than that of liquid oxygen; it has no absorption spectrum and is not magnetic.

* Moissan and Dewar; Chem. Soc. Nov. 1897.

AGRICULTURAL COLLEGE

EXPERIMENTS.

A most characteristic property of fluorine is its affinity for silicon, whether free or combined. In consequence it attacks glass and all substances containing silicon. The hydrogen compound of fluorine—HF—decomposes silica, SiO_2, the F uniting with the Si.

I. Pound up some fluor spar—CaF_2—or cryolite $(NaF)_6$ Al_2F_6, put in a leaden or platinum dish and pour on concentrated sulphuric acid; cover a glass plate with a very thin layer of wax or paraffin, and scratch with a sharp point some design or words through the wax, and then cover the lead or platinum dish containing the mixture of fluoride and acid with it. Place the dish in a warm place for a short time take off the plate—warm over a lamp to melt the wax, which can then be wiped off, and the design eaten or etched into the glass should be visible.

The compound formed between fluorine and silicon is SiF_4, a gas which on contact with water decomposes, gelatinous silica being deposited and a complex acid, hydro-fluo-silicic, 2HF, SiF_4, left in solution.

This acid is sometimes used as a reagent.

CHLORINE, Cl′ and ‴. Atomic weight, 35·37. Specific gravity, liquid = 1·33; gas = 2·449, air = 1.—Chlorine never occurs in the free state, but chiefly in combination with the alkaline metals, as NaCl, KCl, and also with magnesium. It liquefies under a pressure of 6 atmospheres, at 0° C., or at a temperature of 33·0° at 760 mm. The liquid does not conduct electricity and is not very active chemically.

Chlorine at ordinary temperatures is a greenish-yellow gas, which exerts a poisonous and irritating action on the air passages. It dissolves in about half its volume of cold water, and it is commonly used in this form in the laboratory. The water solution on cooling gives crystals of a hydrate.

Chlorine combines with the metals directly, and with many of the non-metallic elements. Its solution in water decomposes on exposure to light, HCl being formed and oxygen liberated. When heated with steam the same decomposition also takes place.

Chlorine will at elevated temperatures expel oxygen from nearly all the metallic oxides. N.B.—The reverse action can take place. See *ante* (Chlorides, &c., heated in air.)

The presence of free chlorine is indicated by its powerful odour, its bleaching action on vegetable colours, its action on potassium iodide and starch (formation of blue iodide of starch), and when in very small quantity, by its secondary oxidising action on a solution of pure ferrous sulphate mixed with ammonium sulphocyanate, NH_4SCy, whereby a deep red colour is produced.

EXPERIMENTS.

I. Mix 12 grms. salt, NaCl, with nine manganese dioxide, MnO_2, introduce into a small flask or wide test-tube; moisten with very little water, and then add about 5 cc. strong sulphuric, and insert a cork with tube. The gas can be best collected in dry cylinders or test-tubes by leading the delivery-tube to the bottom; the tubes may be covered with watch-glasses. Collect three or four test-tubes full by displacement of air by the heavier gas, and also let the gas bubble through water in a test-tube half full. The water will become coloured yellow-green.

II. In one tube of the gas hold a piece of moist blue litmus paper; it becomes immediately bleached, almost before it has time to turn red.

III. In another drop a small piece of tinfoil; it melts down apparently and forms a fuming liquid; in the third tube put a very small piece of real gold leaf; this also will be acted upon and combine with the chlorine, and a yellow liquid will result after adding *one* drop of water. In a fourth tube of the gas insert a lighted wax taper; it will be seen to burn very dimly, and give a copious deposit of carbon as soot.

Chlorine, in fact, unites directly with nearly all the elements, the only striking exceptions being carbon and oxygen and nitrogen.

IV. The solution of chlorine in water will also bleach many ordinary

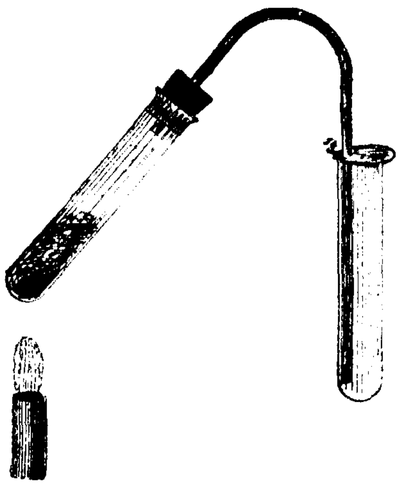


FIG. 20.

colours, such as indigo. Pour a dilute indigo solution into the chlorine water, the blue colour is totally destroyed.

V. Chlorine is stronger chemically than either bromine or iodide. Place a few crystals of potassium bromide in one tube, and some of potassium iodide in another. Now put the delivery tube from the chlorine apparatus into these in succession; one will become reddened by the liberation of bromine, the other nearly black by the liberation of iodine.

BROMINE, Br′ and‴. Atomic weight, 72·77. Melts at 7·3° C.; boils at 59·27° C. under 760 mm. Specific gravity = 3·15.—Bromine occurs mostly in combination with the alkaline metals; and as bromide of silver in Mexico and Chili. At ordinary temperatures bromine is a liquid of deep brown colour almost black; the vapour has a peculiarly disagreeable odour; in the solid form it is dark grey and crystalline, with a semi-metallic lustre. In both states it is a non-conductor of electricity. It is very volatile; a few drops put into a flask speedily fills it with red vapours. Bromine dissolves sparingly in water, more readily in alcohol, on which it slowly reacts, and in all proportions in ether, carbon disulphide, and chloroform.

Bromine does not unite directly with oxygen; but when passed through a red-hot tube with water vapour, oxygen is set free, and hydrobromic acid is formed. Bromine is the only liquid element at ordinary temperatures except mercury. Bromine and its compounds resemble chlorine and its compounds very closely, although it is not so energetic. It bleaches organic colouring matters, but less quickly than chlorine does, and combines directly with metals to form bromides, but its action is less powerful than chlorine. Bromine forms only one compound with hydrogen—namely, hydrobromic acid, but, unlike chlorine, these two bodies do not unite when brought together in sunlight.

EXPERIMENTS AND TESTS.

I. Put a few drops of bromine into a good sized flask; it evaporates without heating and red fumes fill the flask (be careful not to breathe these fumes), hang in the neck of the flask a strip of moistened blue litmus paper, it will turn red and yellow, and then gradually lose its colour or bleach.

II. Hold for a moment a strip of blotting paper that has been dipped in a solution of potassium iodide and starch in the neck of the flask—it will be blued as was the case with iodine and starch. The bromine has liberated the iodine from the potassium and taken its place.

III. Cold solution of soda dissolves bromine to a colourless solution containing hypobromite, bromide and bromate. On evaporating in a dish a white crystalline residue is left.

IV. The solution of soda to which bromine has been added bleaches a piece of litmus paper quicker than bromine itself. This is due to NaBrO.

Bromine added to hot KHO or NaHO solution forms some bromate, which may be obtained in crystals on cooling.

Dilute ammonia dissolves and combines with it, forming bromide. Some nitrogen may be liberated.

Hydrochloric, sulphuric, and nitric acids have no action on bromine.

A strip of lead held in bromine vapour or in a solution of bromine, either in water, or any other solvent, becomes coated with a pale yellow substance, $PbBr_2$.

IODINE, I' and '''. Atomic weight, 126·56. Specific gravity, 4·948. Melting point, 113–115° C. Boiling point, 187° C.—Iodine is a bad conductor of electricity, and possesses a less penetrating odour than chlorine or bromine.

It occurs in combination with the alkaline metals, as iodides of potassium and sodium in kelp; also in several minerals, as iodides of mercury and silver. Much is obtained from Chili saltpetre, where it exists as NaI for the most part.

Iodine is a shining, crystalline, opaque, blackish-grey solid; it crystallises by sublimation in the rhombic system in the form of prisms. It is sparingly soluble in water, more readily soluble in alcohol and ether, easily in carbon disulphide, and in the solution of an iodide.*

Iodine forms only one compound with hydrogen—viz., hydriodic acid. Iodine combines both with chlorine and bromine in at least two proportions.

* These are no doubt compounds.

CHAPTER VIII.

REACTIONS OF THE ACIDS.

A. INORGANIC ACIDS.

CARBONIC ANHYDRIDE, CO_2.—Occurs in the atmosphere and in mineral waters. In the combined state it forms a constituent of many minerals, called carbonates, which have for the most part been enumerated in speaking of the natural compounds in which the different metals occur.

CO_2 may be liquefied by about 75 atmospheres pressure at the ordinary temperature. The liquid evaporates very rapidly, with great absorption of heat, solidifying some of the remaining liquid.

The density of the gas $CO_2 = 1·519$. The liquid at 0° C. = 0·9471. Water = 1. The gas will not support the burning of a taper, but will give up its oxygen to potassium or sodium or magnesium when they are heated in it. When the gas is brought in contact with moist metallic oxides, it is absorbed, with direct formation of carbonates. Calcium or barium oxides in aqueous solution are used for this purpose, as white insoluble precipitates are formed in each case, a very small amount of which is visible.

EXPERIMENTS.

Prepare and collect several large test tubes* of the gas by acting on $CaCO_3$ with dilute HCl in an arrangement like that figured for Chlorine (*which see*). Collect by downward displacement.

I. In one tube introduce a strip of moist blue litmus paper ; it will become claret coloured.

II. Pour lime water into tube ; it becomes milky,

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

III. Introduce burning taper ; it will extinguish, and the gas does not burn.

IV. Introduce burning magnesium ribbon ; it will continue to burn feebly, and black specks or dust, C, will be found along with MgO in tube. On adding HCl the MgO dissolves, leaving the C.

Potassium or sodium heated on a deflagrating spoon and introduced in gas will glow brightly, also leaving black carbon.

DRY REACTIONS.

On ignition some carbonates lose CO_2, others remain unchanged. The carbonates of the fixed alkali metals are very little decomposed

* So-called boiling tubes.

by the strongest heat up to temperatures obtainable in a platinum crucible. At very high temperatures they are somewhat volatilised. The acid carbonates of the alkalies are reduced by heat to normal carbonates, with evolution of CO_2. The carbonates of all other metals are decomposed more or less readily into oxides (or metals), carbonic anhydride (and oxygen) being given off. Barium and strontium carbonates require the strongest white heat for their decomposition; calcium carbonate requires a strong red heat. Most others are readily decomposed on heating.

REACTIONS IN SOLUTION.

All normal carbonates, that is (M'_2CO_3 or $M''CO_3$), may be divided into—

1st. Carbonates which are soluble in water, consisting of the carbonates of the alkali metals, Li, Na, K, Cs, Rb; they possess an alkaline reaction.

2nd. Carbonates which are insoluble in water; this comprises most other normal carbonates.

3rd. Acid carbonates or normal salts in presence of carbonic acid in solution in water are soluble. They are all, however, precipitated on boiling their CO_2 solutions, the CO_2 escaping and a normal carbonate being thrown down.

All carbonates are decomposed by dilute acids—organic or mineral (with the exception of HCy and SH_2). The decomposition is marked by effervescence and evolution of CO_2. On passing the evolved gas into a solution of calcium or barium hydrate, the carbonic anhydride forms a white precipitate (soluble in excess of the gas with formation of acid carbonates).

Metallic sulphites, sulphides, and nitrites are likewise decomposed by dilute acids with evolution of a gas; but the evolved SO_2, SH_2, or nitrous fumes are readily recognised by their characteristic odour or colour. In order to recognise CO_2 in the presence of SO_2 or SH_2, the gaseous mixture may be first passed through a solution of a chromate or bichromate, or bromine-water, or a solution of a cupric or ferric salt, and finally into lime- or baryta-water. (See also methods of separation of CO_2, SO_2, &c., in Tables.)

CARBONIC OXIDE, CO.—Molecular weight, 28. Specific gravity, 0·06799.—This gas burns in air with a blue flame and the production of carbonic anhydride. It is perfectly neutral to vegetable colours, and sparingly soluble in water, which only dissolves about $\frac{1}{40}$th of its bulk at 15° C.

It is rapidly absorbed by cuprous chloride in hydrochloric acid; also by ammoniacal solutions of cuprous salts.

Carbonic oxide is always a result of the reduction of CO_2 by carbon and by most metals at a high temperature.

Some metals as iron, and especially nickel, combine directly with CO,

forming peculiar compounds, as $Ni(CO)_4$ nickel carbonyl.* Potassium also combines directly, the compound being very probably $K_2C_2O_2$ or n(COK); it is decomposed by water very violently.

EXPERIMENTS.

Carbon monoxide can be prepared most easily from formic acid, HCO_2H, by the action of H_2SO_4.

I. The H_2SO_4 is heated gently in a distilling flask or ordinary flask, with cork, tap, funnel and delivery tube, and the formic acid, or a formate, dropped slowly in. The CO is evolved, and may be collected in several tubes over water.

CO is very poisonous, and care must be taken not to breathe any.

II. To one tube introduce blue litmus; it should be unchanged.

III. Introduce a lighted taper; it becomes extinguished, but the gas burns with a blue flame.

IV. Ignite *another* tube of the gas, and then pour in some baryta or lime water.

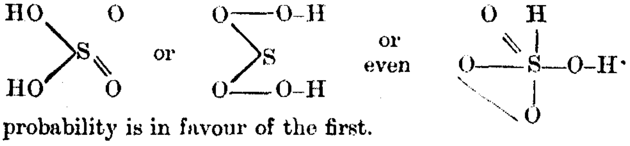
V. Pour lime or baryta water into a tube of the CO. It should not become milky, whilst in IV. it will, owing to $2CO + O_2 = 2CO_2$, the action taking place when CO burns.

VI. Transfer a tube of CO from the water to a small dish in which a solution of Cu_2Cl_2 in HCl has been placed; the liquid will rise in the test tube as the CO is absorbed.

SULPHURIC ACID, H_2SO_4, is the final stage of oxidation of sulphur. It is a very strong acid in this respect; it is capable of displacing, within a moderate range of temperature, almost all other acids from saline compounds.

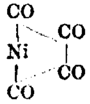
It forms with bases a series of very important salts—the sulphates, some of which have already been enumerated in treating of the natural compounds of the various metals.

The acid is derived from the oxide SO_3, which is produced to a small extent when sulphur is burnt in oxygen. SO_2, sulphur dioxide, also forms SO_3 when heated along with air in contact with platinum. This may be seen by introducing a red-hot platinum wire into a mixture of SO_2 and air or oxygen. It combines with water to form H_2SO_4. What the precise "structure" of this body is is not known. It may be



The probability is in favour of the first.

* The Ni carbonyl compound is formed by gently heating the metal in a stream of CO. The product is a liquid, the vapour of which decomposes below a red heat, bright metallic nickel depositing. It is difficult to imagine the nickel to be more than divalent in this compound, if so, its constitution ought to be,



On a large scale the acid is made by the oxidising action of nitric acid, and oxides of nitrogen, on SO_2. This action can be repeated in a test-tube. Place a few drops of strong nitric acid in a test-tube and then drive in SO_2 gas. Red fumes will first appear due to the action:

$$SO_2 + 2HNO_3 = SO_3 + H_2O + N_2O_4.$$

If the SO_2 supply be continued the red fumes cease and white crystals form on the tube, but if some water be added the crystals will disappear and a further quantity of H_2SO_4 will form. The white crystals are $SO_3N_2O_3$,* which with water give $SO_3H_2O + N_2O_3$. The latter escapes, mixes with air and becomes N_2O_4. If plenty of water be present at the beginning none of these crystals are formed but N_2O_3. In the sulphuric acid manufacture this N_2O_3 is brought in contact with air so that it can act as a carrier of oxygen to the SO_2.

On heating the liquid in the test-tube until whitish fumes begin to form at the mouth of the tube, all the excess of water and oxides of nitrogen are driven off and a few drops of strong sulphuric acid (oil of vitriol) will be left.

The action of this on a piece of filter paper or sugar should be noticed. The paper will turn black and a hole formed in it. The sugar will also blacken. Both actions are due to the abstraction of the oxygen and hydrogen from these organic substances and their combination with the strong acid in the form of water. The substance H_2SO_4 can form a number of definite "hydrates" with water, and the combination is a very energetic one.

DRY REACTIONS.

On heating a sulphate on charcoal, in the reducing flame, together with pure sodium carbonate, sodium sulphide is formed thus:

$$MgSO_4 + 2C + Na_2CO_3 = SNa_2 + MgO + 3CO_2 \dagger$$

The fused mass when treated with an acid (HCl is best generally), gives off SH_2 readily recognised by its odour. When placed on a bright silver coin and moistened with a drop of acid, it produces a black stain of silver sulphide. This reaction on charcoal with Na_2CO_3 applies, however, to all compounds containing sulphur.

Heated by themselves, the sulphates of the fixed alkalies and alkaline earthy metals, as well as of lead, are not decomposed. Acid sulphates ($HKSO_4$, &c.) are converted at a bright red heat into normal sulphates, with evolution of sulphuric acid. Other metallic sulphates become decomposed more or less speedily on

* Or NO_2HSO_4. As a matter of fact several compounds are contained in these white chamber crystals.

† In some cases a sulphide of the metal previously there, as sulphate is produced, although much Na salt is present.

ignition, giving off sulphuric or sulphurous anhydride and oxygen, according to the nature of the metal—*e.g.*:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2.$$
$$CuSO_4 = CuO + SO_2 + O.$$

By distilling in retorts a mixture of ferrous and ferric sulphates an acid known as Nordhausen sulphuric acid is made. Its composition may be simplest represented as $H_2SO_4SO_3$. The action may be:

$$Fe_2(SO_4)_2(OH)_2 = Fe_2O_3 + H_2SO_4 + SO_3.$$

A definite compound can be obtained on cooling in crystals. On warming, however, SO_3 escapes.

REACTIONS IN SOLUTIONS.

A solution of potassium sulphate, K_2SO_4, or any soluble sulphate, may be employed.

Sulphuric acid forms normal and acid sulphates, which are mostly soluble in water, the exceptions being barium and lead sulphates, and a few basic sulphates which, however, are soluble in acids.

$BaCl_2$ gives a white finely divided precipitate of barium sulphate, $BaSO_4$, insoluble in dilute acids. Care must be taken not to have too much free hydrochloric or nitric acid present, lest any of their barium salts be precipitated, barium chloride and nitrate being much less soluble in concentrated acids than in water. If a very dilute solution of a sulphate has to be precipitated, the solution should be heated to boiling, and allowed to stand for some time after the addition of the barium salt.

This reaction distinguishes H_2SO_4 from all other acids except hydrofluosilicic acid, $2HF,SiF_4$, and selenic acid, H_2SeO_4, which are not by any means of common occurrence.

Soluble salts of strontium, calcium, and lead produce white precipitates of strontium, calcium, and lead sulphates, which are more or less soluble in large quantities of water: $CaSO_4$ being the most soluble (in about 500 parts of water), $SrSO_4$ dissolving in 7000 parts of cold water, and $PbSO_4$ in 22,000 parts of water only.

Since barium salts answer every purpose, recourse is rarely had to these reactions in order to detect sulphuric acid. The addition of alcohol (methylated spirit), ensures the complete precipitation of strontium, calcium, and lead sulphates. Most soluble sulphates can, in fact, be precipitated from their aqueous solutions by the addition of strong alcohol, in which they are insoluble.

In order to detect free sulphuric acid, the solution is evaporated to dryness on a water bath, together with a little cane sugar. A blackened or charred residue indicates free sulphuric acid, as no other acid is capable of decomposing cane-sugar in like manner.

An insoluble sulphate can be decomposed by continued boiling

with a concentrated solution of an alkaline carbonate; more readily by fusion with alkaline carbonates (fusion mixture) into a soluble alkaline sulphate, and an insoluble carbonate or oxide of the metal, thus:

$$BaSO_4 + Na_2CO_3 = Na_2SO_4 + BaCO_3.$$
$$PbSO_4 + Na_2CO_3 = Na_2SO_4 + PbO + CO_2.$$

The fused mass is extracted with boiling water, and the insoluble carbonate or oxide separated by filtration from the solution of the alkaline sulphate. The residue is examined as usual for bases, and the solution for sulphuric acid, by acidulating with dilute hydrochloric acid (in order to destroy the excess of alkaline carbonates), and adding barium chloride. Calcium sulphate dissolves in ammonium sulphate containing a little free ammonia; lead sulphate in ammonium acetate or tartrate, or in sodium thiosulphate, or in strong HCl.

SULPHUROUS ACID.—Obtained as a gaseous anhydride, SO_2, whenever sulphur is burnt in air or oxygen, or when metallic sulphides (pyrites, blende, galena, &c.) are roasted with free access of air; also by the partial deoxidation of sulphuric acid by means of metals, such as Cu, Hg, Ag, or charcoal and various organic bodies, sulphur, &c. The gas is readily soluble in water, forming an acid solution, which combines with bases, and forms a series of salts, normal or acid, termed sulphites. They are characterised by the tendency they exhibit to absorb oxygen and become converted into sulphates.

EXPERIMENTS.

SO_2 is very heavy, and can easily be collected in tubes by downward diplacement of air.

Prepare a few tubes of the gas by heating mercury or any other metal (a few grams), with strong sulphuric acid in a small distilling flask or test-tube, with cork and delivery tube.

I. In one introduce blue litmus paper; it becomes red.

II. A burning taper is extinguished, and the gas does not inflame.

III. A piece of ignited magnesium ribbon continues to burn, and some sulphur will be found amongst the MgO.

IV. A piece of filter paper moistened with permanganate will become colourless, moistened with bichromate will become green.

DRY REACTIONS.

Sulphurous anhydride is recognised by its characteristic odour—viz., that of burning sulphur. It combines readily with metallic peroxides, such as MnO_2, PbO_2, with formation of the corresponding sulphates. In order, therefore, to remove SO_2 from a gaseous mixture, the latter may be passed over PbO_2.

Most metallic sulphites are decomposed by heat into sulphates and sulphides, thus:—

$$4Na_2SO_3 = 3Na_2SO_4 + SNa_2.$$

A few sulphites break up, on heating, into oxides and sulphurous anhydride.

REACTIONS IN SOLUTION.

A solution of sodium sulphite, Na_2SO_3, may be employed.

Sulphites are shown by the action of dilute sulphuric or hydrochloric acid upon them, sulphurous anhydride, SO_2, is liberated and readily recognised by its pungent odour.

The only sulphites soluble in water are the alkaline sulphites. Normal barium, strontium, calcium, and magnesium sulphites, though insoluble in water, are dissolved to a great extent by sulphurous acid, with formation of acid sulphites, from which the normal salts are reprecipitated on boiling. (See Carbonates.) They are also soluble in dilute hydrochloric acid (with decomposition); but on the addition of an oxidising agent, such as chlorine water, free iodine, sodium hypochlorite, nitric acid, &c., they are converted into sulphates, some of which are insoluble. (See Sulphuric Acid.)

Commercial sulphites generally contain sulphates as impurities. A precipitate consisting of barium sulphate is, therefore, frequently obtained on adding barium chloride to an acidulated solution of a soluble, or to a dilute hydrochloric acid solution of an insoluble sulphite.

On filtering off the precipitate, and adding chlorine water to the filtrate, a further precipitate is obtained, showing the presence of a sulphite.

Traces of sulphurous acid are distinguished with difficulty by the odour alone, and it is preferable, therefore, to make use of the deoxidising as well as oxidising action which the acid can exert.

1. Sulphurous acid acts as a powerful reducing agent.

$AgNO_3$ gives with sodium sulphite a white precipitate of silver sulphite, Ag_2SO_3, soluble in excess of the alkaline sulphite. The precipitate blackens on heating, owing to the separation of metallic silver, according to the equation :

$$Ag_2SO_3 + OH_2 = Ag_2 + H_2SO_4.$$

$Hg_2(NO_3)_2$ produces a grey precipitate of metallic mercury, thus :

$$Na_2SO_3 + Hg_2(NO_3)_2 + H_2O = Na_2SO_4 + 2HNO_3 + 2Hg.$$

The instances of the reducing action of sulphurous acid are very numerous; its action upon solutions of $AuCl_3$, H_2CrO_4, Fe_2Cl_6, and others, already noticed under the respective metals, need not be repeated here.

2. Under favourable circumstances sulphurous acid acts as an oxidising agent, especially when brought in contact with other more powerful reducing agents, such as nascent hydrogen, SH_2, $SnCl_2$, &c. Thus, by introducing the least trace of SO_2, or a sulphite, into a flask, in which hydrogen is generated from zinc and hydrochloric acid, SH_2 is immediately evolved, along with the hydrogen, and may

be recognised by its odour and action upon lead paper. The change may be expressed as follows :

$$SO_2 + 3H_2 = SH_2 + 2OH_2.$$

SO_2 and SH_2 give rise to the formation of pentathionic acid, with precipitation of white sulphur, according to the equation :

$$5SO_2 + 5SH_2 = \underset{\text{Pentathionic acid.}}{H_2S_5O_6} + S_5 + 4OH_2;$$

Sulphurous acid added to stannous chloride in the presence of hydrochloric acid, gradually precipitates yellow SnS_2. The stannous chloride reduces the sulphurous acid, and the sulphuretted hydrogen and stannic chloride immediately react with the production of SnS_2. The following equations express the changes :

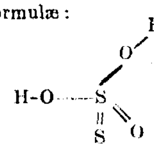
$$(1)\ SO_2 + 3SnCl_2 + 6HCl = 3SnCl_4 + SH_2 + 2OH_2.$$
$$(2)\ SnCl_4 + 2SH_2 = \underset{\text{Yellow stannic sulphide}}{SnS_2} + 4HCl.$$

(See also Phosphorus and Arsenic.)

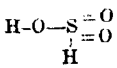
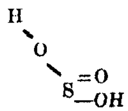
An extremely delicate test for SO_2 is its decolorising action on a solution of permanganate. This should be only of the faintest pink tint ; the liberated gas is decanted into a test-tube and shaken with the permanganate.

THIOSULPHUROUS ACID (thiosulphuric acid).—This acid can only be kept for a short time in a free state in aqueous solution. Its *sodium salt is an important compound, and may be* obtained by boiling a solution of sodium sulphite with sulphur,*

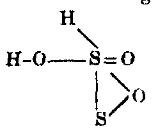
* The action here is similar to that when a sulphide takes up O and becomes a sulphite, or when a sulphite takes up oxygen and forms a sulphate. The sulphur in thiosulphates is undoubtedly in two different states, which may be expressed by the formulæ :



But it is also very probable that sulphites contain one hydroxyl, and the other hydrogen is directly attached to the sulphur :

 the other form being 

This sulphate may correspond to the formula given under sulphuric acid ;



but as before stated, proof is wanting to decide which is most likely.

or by the oxidation of sodium persulphide by contact with the air.

DRY REACTIONS.

All thiosulphates are decomposed on ignition. Alkaline thiosulphates leave a polysulphide and a sulphate, thus:

$$4Na_2S_2O_3 = S_5Na_2 + 3Na_2SO_4.$$

Some sulphur burns off if the heating take place in air.

REACTIONS IN SOLUTION.

A solution of sodium thiosulphate, $Na_2S_2O_3$ is the commonest and most easily soluble salt.

Most thiosulphates are soluble in water (barium thiosulphate is difficultly soluble in cold water), and their solutions may, with few exceptions, be boiled without decomposition. Calcium thiosulphate is gradually decomposed on boiling, the precipitate consisting of calcium sulphate and sulphur. When thiosulphates are treated with sulphuric or hydrochloric acid, sulphurous anhydride is evolved and sulphur is separated. The precipitated sulphur is yellow, and not white, as is usually the case when sulphur separates in chemical reactions. The change characterises thiosulphates.

The same instability of the sulphur atom, occupying the place of an atom of oxygen in sulphuric acid, is observed when thiosulphates come in contact with salts, whose metals form insoluble sulphides.

$AgNO_3$ gives a white precipitate of silver thiosulphate, $Ag_2S_2O_3$, soluble in sodium thiosulphate, which speedily turns yellow, then brown, and lastly black (SAg_2), especially on the application of heat, thus:

$$Ag_2S_2O_3 + OH_2 = SAg_2 + H_2SO_4.$$

Mercurous nitrate and lead acetate give similar precipitates which are decomposed by heat into Hg_2S or PbS, and sulphuric acid.

$SnCl_2$ gives a brown precipitate of SnS.

Thiosulphates, like sulphites, are readily oxidised, but yield, under certain conditions, oxygen to more powerful reducing agents, and thus become oxidising agents.

Free chlorine, sodium hypochlorite, ferric chloride, &c., oxidise thiosulphates in the presence of water completely to sulphates, even when cold, thus:

$$Na_2S_2O_3 + 4Cl_2 + 5OH_2 = 2HNaSO_4 + 8HCl.$$
$$Na_2S_2O_3 + 4ClNaO + OH_2 = 2HNaSO_4 + 4NaCl.$$

$Na_2S_2O_3$ gives with Fe_2Cl_6 at first a reddish-violet coloration (difference between sulphites and thiosulphates), but on standing,

the solution is slowly decolorised (more readily on heating), with formation of $FeCl_2$, thus:

$$Na_2S_2O_3 + 4Fe_2Cl_6 + 5OH_2 = 2NaHSO_4 + 8FeCl_2 + 8HCl.$$

Nascent hydrogen reduces thiosulphates, and sulphuretted hydrogen is evolved:

$$Na_2S_2O_3 + 4H_2 + 2HCl = 2SH_2 + 3OH_2 + 2NaCl.$$

Some sulphur is always precipitated as well.

Sodium thiosulphate is a useful solvent for haloid silver salts (for which it is much used in photography), Hg_2Cl_2 and $PbSO_4$. Calcium thiosulphate, CaS_2O_3, is used as an agent for removing the last traces of chlorine in the bleaching of paper pulp, and from fabrics bleached by means of bleaching powder, to prevent their deterioration by the traces of chlorine which they are apt to retain. It has on that account received the name of antichlor. The free hydrochloric acid which is formed in the reaction is neutralised by passing the fabrics through a weak alkaline bath. Sulphites are now used for this purpose.

The property of sodium thiosulphate of dissolving AgCl has found an important metallurgical application in the removal of silver from poor argentiferous ores, after they have undergone the process of roasting with common salt, which converts the silver into AgCl, insoluble in water.

A still lower oxide of sulphur, SO or S_2O_2 the hydrate of which is probably H_2SO_2, is obtained in combination, when metallic zinc is placed in a solution of SO_2 in water. No gas is evolved at first, but the solution becomes coloured brown, a zinc salt,* which rapidly decomposes, being formed. It is a very powerful reducing agent, precipitating the metal from salts of copper or lead, bleaching indigo and other colouring matters, &c.

HYDROSULPHURIC ACID (sulphuretted hydrogen), SH_2, is obtained as a colourless gas by the decomposition of certain metallic sulphides, such as FeS, ZnS, Sb_2S_3, by means of sulphuric or hydrochloric acid. It is characterised by a fœtid odour, resembling that of rotten eggs. It is absorbed by cold water, forming sulphuretted hydrogen water, which reddens blue litmus paper feebly. Hydrosulphuric acid exchanges its sulphur for the oxygen of most metallic oxides, forming water and metallic sulphides, and is on this account a most valuable reagent. Many native sulphides—*e.g.*, iron pyrites, galena, cinnabar, zinc blende—are met with in vast masses, and constitute the principal minerals from which the metals are extracted.

* Very little is known with certainty about this action or the body produced. Metallic zinc dissolves also in hydrogen sodium sulphite; the reaction may be:

$$2(NaHSO_3) + Zn = \underbrace{H_2O + Na_2ZnS_2O_4}\ (?)$$

DRY REACTIONS.

Metallic sulphides are acted upon in various ways when submitted to heat. Some are decomposed, when heated in a close vessel, into metal and sulphur, *e.g.*, Au_2S_3; some sulphides, such as PtS_2, FeS_2, Sb_2S_5, SnS_2, PbS, yield up a portion of their sulphur, and are reduced to PtS, Fe_3S_4 or FeS, Sb_2S_3, SnS, Pb_2S; others sublime without decomposition, such as As_2S_3 (*orpiment*), *HgS* (*cinnabar*). A great number of metallic sulphides remain, however, undecomposed, when heated out of contact with atmospheric air.

Most sulphides undergo a change when roasted in a tube open at both ends. SAg_2 leaves metallic silver (usually also a little Ag_2SO_4); the sulphur, combining with oxygen, passes off as SO_2; some sulphides leave a metallic oxide, *e.g.*, SnS, Sb_2S_3, Bi_2S_3; others again, such as the sulphides of the alkalies and alkaline earthy metals, are converted into sulphates. Lead sulphide (galena) is converted into a mixture of oxide and sulphate; cupric sulphide, when roasted at a high temperature, yields SO_2 and CuO; at a lower temperature $CuSO_4$. FeS and other sulphides of the iron group are partially converted into sulphates, which, on the application of a stronger heat, lose their acid, leaving metallic oxides. Many native metallic sulphides are distinguished for their metallic lustre, such as iron and copper pyrites, galena, grey antimony, &c.

REACTIONS IN SOLUTION.

Alkaline and alkaline earthy sulphides are soluble in water (CaS and MgS are only sparingly soluble). Dilute hydrochloric acid decomposes them readily into metallic chlorides and SH_2. All other sulphides are insoluble in water. FeS, MnS, ZnS, are decomposed by dilute hydrochloric acid with evolution of sulphuretted hydrogen. Others require concentrated hydrochloric acid, such as NiS, CoS, Sb_2S_3, SnS_2, PbS. The rapidity of the action of acids on sulphides depends very much on the physical state of the latter. Sulphides which are insoluble, or difficultly soluble, in concentrated hydrochloric acid, such as Bi_2S_3, CuS, SAg_2, PbS, As_2S_3, are decomposed by concentrated nitric acid; they are generally oxidised into sulphates—at first with separation of sulphur, which by prolonged digestion is for the most part converted into sulphuric acid. Others, such as HgS, PtS_2, Au_2S_3 (As_2S_3) dissolve easily only in aqûa regia, or hydrochloric acid and potassium chlorate, with separation of sulphur and formation of sulphuric acid, and of a metallic chloride. On dissolving PbS, SnS_2, Sb_2S_3, As_2S_3, in concentrated nitric instead of hydrochloric acid, they are converted principally into $PbSO_4$, SnO_2, Sb_2O_4, H_3AsO_4.

To detect SH_2 (*in an aqueous solution*) *or a soluble sulphide* (a solution of ammonium sulphide may be conveniently employed for illustration) add a solution of a salt of cadmium, lead, or silver, which gives by double decomposition a characteristic precipitate of a metallic sulphide; fine yellow for cadmium, black for lead or silver salts.

To analyse a sulphide decomposable by hydrochloric acid, the evolved sulphuretted hydrogen gas is made to act upon lead paper or is passed through a solution of a lead salt. (Iron pyrites and copper pyrites give off SH_2 in the presence of zinc only.)

Sulphides which are not decomposed by hydrochloric acid yield sulphur on treatment with nitric acid or aqua regia, and must be recognised by this and the products of decomposition, such as SnO_2, $PbSO_4$, as well as the reactions which they give when examined in the dry way.

Many native sulphides, such as fahl ore, &c., are expeditiously examined by heating the finely powdered mineral in a hard glass tube, in a current of dry chlorine gas, when the metals are converted into chlorides and the sulphur into volatile chloride of sulphur, which is decomposed on being passed into water, HCl, H_2SO_4, and S resulting.

To detect a soluble alkaline sulphide in the presence of free SH_2, add a few drops of a solution of sodium nitroprusside. This reagent does not affect free SH_2, but gives a fine purple colour with the merest traces of soluble sulphides. The colour disappears only after some time. It does not show in the presence of free caustic alkalies.*

A mixture containing a soluble sulphide, thiosulphate, sulphite, or sulphate, may be examined by adding cadmium carbonate, $CdCO_3$, to the aqueous solution. Filter after agitation, dissolve the excess of $CdCO_3$ in the precipitate by means of dilute acetic acid; a residue of yellow CdS indicates the presence of a sulphide. Add $BaCl_2$ to the filtrate; a precipitate is obtained consisting of $BaSO_4$, and $BaSO_3$. Filter off; digest the precipitate with dilute hydrochloric acid, and filter. A white residue shows the presence of a sulphate. Add chlorine water to the filtrate; a precipitate of $BaSO_4$ indicates the presence of a sulphite. The filtrate from the $BaCl_2$ precipitate is examined for thiosulphates by the addition of HCl and boiling. A precipitate of yellow sulphur and the odour of SO_2 indicate the presence of a thiosulphate.

To remove SH_2 from a gaseous mixture of CO_2 and SH_2, shake up a solution of cupric or cadmium chloride with the gases.

EXPERIMENTS.

SH_2 being heavier than air can be collected in tubes by downward displacement. The most convenient mode of preparation is by acting on FeS with HCl. It can be done in a flask or tube, with delivery tube. Aluminium sulphide is also convenient as it is decomposed by water.

I. Blue litmus paper, when moist, is reddened.

II. A taper is extinguished, but the gas burns forming water, which will make

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* Sodium nitroprusside, $Fe(CN)_5NOCNNa_2$, may be readily prepared by heating a few crystals of potassium ferricyanide with concentrated nitric acid in a test tube until red fumes are copiously evolved, then diluting with water, and neutralising with sodium carbonate. The solution may be used directly for testing for sulphides. (Playfair.)

a deposit of moisture on a cold substance, and a little SO_2 and some sulphur will be deposited on the sides of the tube as the flame sinks.

III. A piece of paper moistened with lead acetate is turned black on immersion in the gas; a silver coin placed on the top of the tube will also be blackened.

NITRIC ACID, HNO_3, is obtained as a colourless, highly corrosive distillate when nitrates are gently heated with strong sulphuric acid, and the vapour, which arises, condensed. It is characterised by the facility with which it parts with its oxygen, and it is on this property that the detection of nitric acid or a nitrate depends. Crude nitric acid is yellow, because of partial decomposition into nitrous acid, and presence of oxides of nitrogen.

DRY REACTIONS AND EXPERIMENTS.

Most nitrates fuse readily when heated. All are decomposed when heated to a high temperature. The decomposition products vary with the nature of the base, and to some extent with the temperature employed, an oxide of nitrogen and oxygen generally being given off. Thus, ammonium nitrate, NH_4NO_3, breaks up into ON_2 and $2(OH_2)$; potassium or sodium nitrate into nitrite (always contaminated, however, with nitrate and caustic alkali) with liberation of oxygen, and ultimately, on the application of a stronger heat, into oxide or peroxide—nitrogen and oxygen being given off; others, such as lead nitrate, into O and N_2O_4, leaving the oxide of the metal. When heated together with bodies capable of taking up oxygen, such as carbon, charcoal, alkaline cyanides, sulphur, or phosphorus, the decomposition becomes explosively violent, and free nitrogen gas only is liberated. (Chlorates explode in like manner, but leave metallic chlorides.)

REACTIONS IN SOLUTION.

With the exception of a few basic salts, nitrates are readily soluble in water; hence nitric acid cannot be detected in the usual way—that is by producing precipitates by double decomposition. When acted upon by reducing agents, *e.g.*, nascent H, the deoxidation of the acid may be partial, to some of the lower oxides of nitrogen, or complete to nitrogen, in which case the nascent hydrogen is capable of combining with it to form ammonia.

Quite a number of intermediate products can be obtained from the action of nascent hydrogen on nitrates.

N_2O_4 or NO_2
N_2O_3
N_2O_2 or NO
N_2O
NH_2OH
NH_3.

1st. Reactions in which nitric acid is reduced to lower oxides of nitrogen.

Dilute nitric acid, or a solution of potassium nitrate, KNO_3, may be employed.

Nitric acid and nitrates are decomposed when heated with concentrated hydrochloric acid (or a chloride when heated with nitric acid). *Nitrosyl chloride, NOCl, and chlorine are evolved, and the* liquid acquires the power of dissolving gold leaf or platinum-foil (see these metals) because of the chlorine produced. (Chlorates, bromates, iodates, chromates, and permanganates also evolve chlorine when treated with hydrochloric acid.)

Pour some concentrated sulphuric acid (free from nitric acid) upon a little potassium nitrate, in a dry test tube, see that the mixture is cool, and then add gradually a solution of ferrous sulphate so that it lies upon the sulphuric acid – not mixing with it, or better, a few crystals of ferrous sulphate. A ring is seen to form at the point of contact of the two layers, or around the crystals, of a violet, red, or dark-brown colour, according to the quantity of the nitrate present. The coloration is increased by *very slight* agitation, but it disappears on heating. This is owing to the formation of a transient compound of the ferrous salt with N_2O_2; $(4FeSO_4,N_2O_2)$. The other three atoms of oxygen from two molecules of nitric acid oxidise six molecules of ferrous into three molecules of ferric sulphate, $Fe_2(SO_4)_3$. This is the usual method by which nitric acid is detected. The change may be expressed thus:

$$10FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4FeSO_4,N_2O_2 + 4OH_2.$$

A solution of a nitrate, when added to a hot solution of indigo in sulphuric acid (sulphindigotic acid), changes the blue colour of the indigo to yellow. (Free chlorine and other oxidising agents also bleach indigo.)

Metals, Cu, Ag, Zn, Pb, or Hg are dissolved by nitric acid with evolution of ruddy fumes, and also by a mixture of a nitrate with strong sulphuric acid.

A similar reaction takes place when copper filings are mixed with a nitrate and hydrogen potassium sulphate and fused in a test tube or crucible.

2nd. Reactions in which nitric acid is entirely reduced, and its nitrogen converted into ammonia.

All nitrates when fused with caustic potash, lime, or soda-lime, and some non-nitrogenous organic substance, such as sugar or starch, evolve ammonia.

The gas may be readily recognised by its odour, or action upon red litmus paper. The reaction may be done in a test tube.

Nascent hydrogen, produced by the action of KHO upon metallic zinc, iron, or aluminium, gives rise, in the presence of a nitrate, to the formation of ammonia, thus:

$$(1)\ Zn + 2KHO = Zn(KO)_2 + H_2.$$
$$(2)\ KNO_3 + 4H_2 = NH_3 + KHO^* + 2OH_2.$$

* The KHO represented here is in practice further changed by the metal employed.

When stannous chloride, hydrochloric acid, and a nitrate are heated together, the tendency of the stannous chloride to combine with two more atoms of chlorine to form stannic chloride, aided by the oxidising action of nitric acid upon the hydrogen, breaks up hydrochloric acid, with formation of stannic chloride and ammonia, thus:

$$4SnCl_2 + KNO_3 + 10HCl = 4SnCl_4 + NH_4Cl + KCl + 3OH_2.$$

Nitrates gently heated with ammonium salts, as KNO_3 and NH_4Cl, give nitrous oxide as one product:

$$KNO_3 + NH_4Cl = KCl + H_2O + N_2O.$$

N_2O supports the burning of a glowing match.

To detect free nitric acid in the presence of a nitrate, evaporate the solution on a water-bath with quill cuttings or white wool or silk. Nitric acid colours these substances yellow.

NITROUS ACID, HNO_2.—Both the acid and anhydride are marked by their proneness to undergo decomposition, in the presence of water, into nitric acid and nitric oxide.

DRY REACTIONS.

Nitrites fuse and are decomposed on ignition into oxides, with evolution of nitrogen and oxygen. Mixed with carbon, potassium cyanide, sulphur, and other oxidisable bodies, nitrites deflagrate like nitrates, with which they have, in fact, most of the dry reactions in common.

REACTIONS IN SOLUTION.

All nitrites are soluble in water; silver nitrite, $AgNO_2$, although readily soluble in hot water, is somewhat difficultly soluble in cold water (300 parts), and serves for the preparation of pure nitrites, by double decomposition with neutral soluble chlorides. Dilute acids liberate N_2O_2 and convert a portion of the nitrite into nitrate, thus:

$$3KNO_2 + H_2SO_4 = N_2O_2 + KNO_3 + K_2SO_4 + OH_2.*$$

The reactions by which the presence of nitrous acid can be readily recognised, may be divided into two classes:

1st. Reactions in which the acid acts as an oxidising agent.

SH_2 decomposes aqueous solutions of alkaline nitrites, with formation of N_2O_2 (of NH_3 when the reaction goes on for some time) and alkaline sulphides, thus:

$$2KNO_2 + 2SH_2 = N_2O_2 + 2OH_2 + S_2K_2.$$

*** As performed in the usual way red fumes are always produced due to formation of N_2O_3 and NO_2 by contact of the N_2O_2 with air.**

In acid solutions the decomposition is accompanied by a copious separation of sulphur.

Acid solutions of ferrous salts are turned dark brown on addition of a nitrite, owing to the absorption of N_2O_2 gas by a portion of the unoxidised ferrous salt. On the application of heat N_2O_2 is evolved, thus:

$$2FeCl_2 + 4HCl + 2KNO_2 = Fe_2Cl_6 + 2KCl + N_2O_2 + 2OH_2.$$

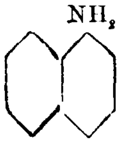
Ammonium nitrite, $NO_2(NH_4)$, breaks up, on the application of heat, into N and OH_2. Nitrites containing fixed bases are decomposed in like manner on the addition of an ammonium salt, thus:

$$(NH_4)_2CO_3 + 2KNO_2 = N_4 + 4OH_2 + K_2CO_3.$$

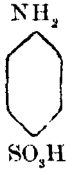
KI and starch solution give in the presence of a nitrite and a dilute acid blue iodide of starch. (See also HI.)

When a very dilute solution of a nitrite—say a polluted well water—is added to a cold saturated solution of sulphate of diamidobenzoic acid and the nitrous acid liberated with a few drops of dilute acid (H_2SO_4), *the solution acquires an intense yellow colour*. As little as $\frac{1}{5}$ mgr. of N_2O_3 diffused in one litre of water can thus readily be discovered.

The HCl compound of phenylenediamine is even more delicate in its indication, a rosy colour being produced. Possibly the most delicate test for nitrous acid is a mixture of *a*-naphtylamine and sulphanilic acid dissolved in a slight excess of H_2SO_4. Exceedingly minute quantities of HNO_2 give with this reagent a lovely rosy red coloration due to the formation of a diazo derivative.



= *a*-naphtylamine = $C_{10}H_7NH_2$.



= sulphanilic acid = $C_6H_4NH_2SO_3H$.

The reagent should be made by dissolving equivalent weights of *a*-naphtylamine and sulphanilic acid in moderately strong H_2SO_4. This solution should be colourless. A few drops only of the solution to be tested is diluted with 20 to 50 times as much water and one cubic centimetre of the *a*-naphtylamine solution added. A rosy pink colour should appear within ten minutes.

The test is too delicate for most ordinary purposes.

2nd. Reactions in which the acid acts as a reducing agent, and is converted into nitric acid, thus:

$$2HNO_2 + O_2 = 2HNO_3.$$

$AuCl_3$ and Hg_2Cl_2 give metallic gold and grey metallic mercury.

$K_2Mn_2O_8$ oxidises nitrites into nitrates in the presence of a mineral acid (H_2SO_4), and the permanganate solution is rapidly decolorised.

Potassium dichromate is reduced under similar conditions to a green salt of chromium. Nitrates are not affected by potassium permanganate or alkaline chromates.

PbO_2 converts HNO_2 into HNO_3, but does not act upon very dilute HNO_3.

HYDROCHLORIC ACID. Gaseous hydrochloric acid, HCl, is readily absorbed by water, and forms one of the most useful acids. Chlorides are an important class of chemical compounds and are very widely distributed in Nature.

Some chlorides are liquid at the ordinary temperature and can be distilled without decomposition, such as $SnCl_4$, PCl_3 and CCl_4; $SbCl_3$ is a soft, white, crystalline solid which distils at 225° C.; others are solid, fusible and non-volatile at a moderate heat, but may be vaporised at any high temperature such as a porcelain furnace or an oxy-hydrogen flame. Such are $AgCl$, $PbCl_2$, $BaCl_2$, KCl, $NaCl$.

EXPERIMENTS.

I. HCl is given off as a gas when a chloride is treated with strong H_2SO_4. NaCl, sodium chloride, is the substance used for the source of chlorine, hydrochloric acid, and of sodium compounds. Arrange a large test tube or flask with delivery tube, charge with common salt and drop on to this strong H_2SO_4. The gas will escape and be nearly dry.

FIG. 21.

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

It is not necessary to heat the substances. Several dry tubes may be filled by the gas by downward displacement and then covered with a waxed plate.

N.B.—The most convenient covering for a test-tube in which a gas has been collected is a watch glass in which some paraffin wax has been melted and allowed to become almost solid and the wax then gently pressed on the top of the test-tube.

Place in the tube a piece of well dried blue litmus, notice the colour hardly changes until moisture has been absorbed, also notice the white fumes when the gas comes in contact with moist air.

II. Introduce a burning taper. It is extinguished and the gas does not burn.

III. Pour in lime water; remains clear.

IV. Introduce quickly into a tube of the dry gas a little zinc or magnesium filings or aluminium foil, shake up for a minute holding the waxed cover tightly on and then test the gas in the tube with a flame.

It should burn with a flame like hydrogen because:

$$Mg + 2HCl = H_2 + MgCl_2.$$

V. A tube of the gas should be inverted with the mouth under cold water and then the cover removed; water should enter the tube, almost filling it. Litmus placed in this water is reddened.

VI. A gram or so of MnO_2, or $K_2Mn_2O_8$, or PbO_2 in powder dropped into a tube of HCl liberates a little chlorine. After standing a minute or so a piece of blue litmus should be bleached on placing in the gas.

REACTIONS.

Upon ignition certain chlorides such as $AuCl_3$, $PtCl_4$, are decomposed with evolution of chlorine gas, first into AuCl and $PtCl_2$, which are almost insoluble in water, and finally into Au and Pt. Magnesium chloride is decomposed by heat, in the presence of water, into magnesium oxychloride, Mg_2OCl_2, with formation of HCl. Anhydrous ferric chloride, when heated in contact with air, is decomposed into Fe_2O_3 and $3Cl_2$. Similarly with aluminic chloride which also decomposes very energetically with water and bodies containing hydroxyl, or with certain hydrocarbons and halogen compounds.

Heated in a bead of microcosmic salt saturated with cupric oxide, *chlorides impart a blue colour to the outer flame*, owing to the formation of volatile $CuCl_2$.

When a dry chloride is mixed with potassium dichromate and concentrated sulphuric acid, and gently heated, a deep brownish-red gas, called chlorochromic acid, CrO_2Cl_2, is formed and can be collected in a receiver. It is a deep red, almost black liquid. The reaction taking place is expressed by the equation:

$$4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = \underset{\text{Chlorochromic acid or chromyl-chloride}}{2CrO_2Cl_2} + 2Na_2SO_4 + K_2SO_4 + 3OH_2.$$

This liquid is decomposed, on mixing with water, into chromic and hydrochloric acids, thus:

$$CrO_2Cl_2 + 2OH_2 = H_2CrO_4 + 2HCl;$$

or by aqueous ammonia or potassium hydrate into the corresponding salts. The presence of chromic acid, and *indirectly* of hydrochloric acid, is inferred from the *yellow precipitate which a lead salt produces* with these solutions.

The reaction may be employed for recognising a chloride in the presence of a bromide or iodide. The two latter are liberated as Br and I respectively, and on the addition of sodium or potassium hydrate are dissolved to a colourless solution.

To make sure in case of a mixture it is better to test for Cr in the aqueous solution of the distillate either by the hydrogen-peroxide reaction or with a bead of sodium carbonate. (*See* CHROMIC ACID.)

Chlorides may be divided into:

1st. Chlorides insoluble in water, such as AgCl and Hg_2Cl_2, which are quite insoluble; $PbCl_2$, soluble in 135 parts of cold water, readily soluble in boiling water; and Cu_2Cl_2, almost insoluble

EXPERIMENTS AND REACTIONS IN SOLUTION.

A solution of potassium chlorate may be employed.

All chlorates are soluble in water.

Concentrated sulphuric acid decomposes potassium chlorate even in the cold, a reddish liquid and greenish-yellow gas, called chloric peroxide, ClO_2, being formed, which is recognised by its suffocating odour. On the application of heat a violent explosion occurs due to the resolution of ClO_2 into chlorine and oxygen. A single crystal only of the chlorate should be employed, and the test-tube should be held with its mouth turned away from the operator. The change may possibly be expressed by the equations:—

$$2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3;$$
$$2(HClO_3) = H_2O + Cl_2O_4 + O.$$

A chlorate dropped into *hot* sulphuric acid gives off a mixture of chlorine and oxygen gases. This is quite safe.

Strong hydrochloric acid, especially when heated, decomposes potassium chlorate, giving off a mixture of chloric peroxide and free chlorine, thus:

$$8KClO_3 + 24HCl = 6ClO_2 + 9Cl_2 + 8KCl + 12OH_2.$$

A solution of indigo (sulphindigotic acid) is decolorised on the addition of a chlorate and dilute sulphuric acid, by a reaction analogous to that produced by free nitric acid.

PERCHLORIC ACID, $HClO_4$.—Perchlorates are more stable than chlorates. Concentrated sulphuric acid fails to decompose them when cold and with difficulty only on heating. (Distinction from chlorates.) Hydrochloric, nitric, and sulphurous acids do not decompose aqueous solutions of perchlorates, nor is indigo solution decolorised. All perchlorates are soluble in water, most of them freely. Potassium perchlorate is sparingly soluble in cold water, and insoluble in alcohol. It resembles potassium permanganate in some respects.

Some potassium perchlorate, $KClO_4$, is formed when potassium chlorate is heated until *some* oxygen has been given off. The residue then contains a mixture of chlorate, chloride and perchlorate. Enough perchlorate can be obtained by heating a few grams $KClO_3$ in a tube, until it has melted and the oxygen commences to come off somewhat rapidly. The tube may then be dropped carefully into water. It will break up. The water should then be boiled up, filtered from the glass particles and allowed to crystallise, after evaporation if necessary, and the crystals boiled with HCl until no more chlorine or ClO_2 is evolved and finally recrystallised.

In order to distinguish a nitrate in the presence of a chlorate, mix the substance with Na_2CO_3, if other bases than potassium and sodium are present, and ignite until the evolution of oxygen nearly ceases,

and test the residue for nitrous acid. The effect of the ignition upon the chlorate is to change it into chloride, and the nitrate into nitrite to some extent. The Cl may be tested for (by adding HNO_3 and $AgNO_3$ to a portion), but this is not evidence of the presence of a chlorate in the original substance, unless chlorides are proved absent. Nitrites (alkaline) will withstand a higher temperature than chlorates.

To apply this test for chlorates in the presence of chlorides, an excess of Ag_2SO_4 must be first added to the solution, and the filtrate from the AgCl may then be mixed with Na_2CO_3, evaporated to dryness, and treated as above.

HYPOCHLOROUS ACID, ClHO.—The salts which this acid forms possess considerable interest, on account of the powerful bleaching action which they exert in the presence of acids. Sodium and calcium hypochlorites are obtained along with the corresponding chlorides, by passing chlorine through a cold solution of the carbonate or hydrate. An important compound closely related to the hypochlorites is the so-called calcium chlorohypochlorite (a constituent of chloride of lime or bleaching powder), which appears to be formed according to the equation:

$$Ca(HO)_2 + Cl_2 = Ca(OCl)Cl + OH_2.$$

Hypochlorites are gradually decomposed on exposure to air with liberation of chlorine owing to the action of carbonic anhydride contained in air, and it is on this account that hypochlorites are of such great value as disinfectants and bleaching agents.

DRY REACTIONS.

Hypochlorites, when heated, are converted into chlorates and chlorides, thus:

$$6Ca(OCl)Cl = 5CaCl_2 + Ca(ClO_3)_2.$$

REACTIONS IN SOLUTION.

Calcium or sodium hypochlorite, ClNaO, are the commonest, the former especially, and is known as "chloride of lime."

All hypochlorites are soluble in water. Their aqueous solutions when acidified bleach vegetable colours. On heating or evaporating dilute solutions of hypochlorites, they are partly decomposed into chlorides and chlorates. Dilute acids decompose them with evolution of chlorine. (Distinction between hypochlorites and chlorates.) Hypochlorites in solution yield oxygen to readily oxidisable substances, and become converted into chlorides; thus:

As_2O_3 is oxidised to As_2O_5.
$MnCl_2$ " " MnO_2.
PbO " " PbO_2.
PbS " " $PbSO_4$.
$\begin{cases} OCOH \\ OCOH \end{cases}$ " " $2CO_2 + OH_2$.

Indigo and litmus are readily decolorised.

HYDROBROMIC ACID, HBr.—Bromides are decomposed by H_2SO_4 in a similar manner to chlorides, and *some* HBr in a gaseous state is evolved. A secondary action commences, however, very quickly, by which some of the HBr becomes oxidised at the expense of the H_2SO_4, and bromine is liberated. *H_2SO_4 does not oxidise HCl.*

$$(\alpha)\ NaBr + H_2SO_4 = NaHSO_4 + HBr$$
$$(\beta)\ 2HBr + H_2SO_4 = 2H_2O + SO_2 + Br_2.$$

A mixture, therefore, of bromine vapour and HBr gas is usually obtained. A few bromides, as those of AgBr, Hg_2Br_2, are decomposed only slowly by H_2SO_4, but completely by heating with $KHSO_4$.

DRY REACTIONS.

Most bromides remain unaltered when ignited; others are volatilised without decomposition. $AuBr_3$ and $PtBr_4$ are decomposed upon ignition into metal and bromine, which volatilises. Many bromides are changed upon ignition with free access of air, being converted into oxides and free bromine; others, such as Al_2Br_6, &c., are decomposed, on evaporation of their aqueous solutions, into oxides and hydrobromic acid. KBr and NaBr are converted, to a great extent, into KCl and NaCl, on repeated ignition with ammonium chloride. When fused with hydrogen-potassium sulphate bromides are decomposed into sulphates with evolution of sulphurous anhydride and bromine.

Bromides heated before the inner flame of the blowpipe on a bead of microcosmic salt, in which a little cupric oxide has been diffused, impart a blue colour to the flame, which passes into green, especially at the edges. The difference between chlorides and bromides in this reaction is not very marked.

REACTIONS IN SOLUTION.

A solution of potassium bromide, KBr, may be employed.

Metallic bromides can be divided into:

1st. Bromides which are insoluble in water, such as AgBr, Hg_2Br_2, $PbBr_2$ (less soluble in water than $PbCl_2$), and—

2nd. Bromides which are soluble in water, comprising most other bromides, and—

3rd. Bromides, *e.g.*, $SbBr_3$, $BiBr_3$, which are decomposed by water into insoluble oxybromides SbOBr, BiOBr, and hydrobromic acid. They resemble in this respect the corresponding chlorides.

In order to detect hydrobromic acid or a soluble bromide, add a solution of silver salt to the solution, when a yellowish-white precipitate of silver bromide, AgBr, is formed, which is insoluble in dilute nitric acid, somewhat soluble in concentrated ammonium hydrate, readily soluble in potassium cyanide or sodium thiosulphate.

Insoluble AgBr is best decomposed by heating in an ignition-tube with alkaline carbonates (free from chlorides). The aqueous extract is tested for hydrobromic acid, and the insoluble residue for silver.*

In the absence of any well marked distinguishing features in the silver bromide precipitate, it is preferable to liberate bromine from soluble bromides, and to cause the reddish-brown vapour to act upon starch paste with formation of yellowish bromide of starch.

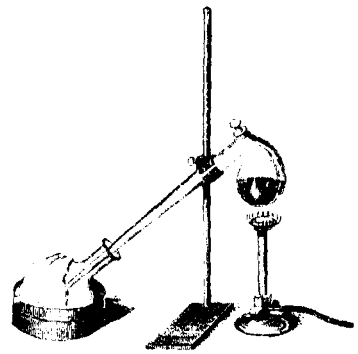


FIG. 22.

Nitrous acid (or a nitrite and dilute sulphuric acid) does not liberate any bromine from pure soluble bromides. (Distinction between bromides and iodides.) All bromides are, however, decomposed by chlorine, with evolution of bromine, which remains dissolved in the aqueous solution. On shaking with a little chloroform or bisulphide of carbon, the bromine is taken up, and forms a yellowish-red liquid, which sinks in the saline aqueous solution.

Bromine is obtained from natural bromides, such as potassium, magnesium, and calcium bromides, by reactions analogous to those employed for the preparation of chlorine from common salt: for instance, by distilling with manganic oxide and strong sulphuric acid, thus:

$$2KBr + MnO_2 + 2H_2SO_4 = Br_2 + K_2SO_4 + MnSO_4 + 2OH_2,$$

or by distilling a bromide with potassium dichromate and sulphuric acid, thus:

$$6KBr + K_2Cr_2O_7 + 7H_2SO_4 = 3Br_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7OH_2.$$

A mixture of a bromide and manganic oxide, or potassium dichromate is introduced into a tubulated retort (Fig. 22), with concentrated sulphuric acid diluted with its own weight of water, and gently heated over a gas flame. The reddish-brown vapour of

* AgBr is very soluble in solutions of KBr, NaCl, HCl, KI. Water precipitates it again from these.

bromine passes over, and condenses in a flask (which should be kept cold by a stream of water, or better still in a vessel surrounded with ice (to a reddish-brown heavy liquid).*

Concentrated sulphuric acid alone evolves hydrobromic acid, together with bromine and sulphurous anhydride, as a *part* of the HBr is oxidised by the sulphuric acid (*ante*).

Concentrated nitric acid evolves bromine, together with nitrous fumes, thus:

$$2KBr + 4HNO_3 = Br_2 + 2KNO_3 + N_2O_4 + 2OH_2.$$

In the last two reactions the sulphuric and nitric acids act as oxidising agents, performing in fact the functions of the manganic oxide and potassium dichromate in the former reactions.

It is obvious that the hydrogen may also be removed from hydrobromic acid (or the metal from a metallic bromide) by other oxidising agents, such as permanganates and metallic peroxides, in the presence of an acid.

Bromine (like chlorine) is an indirect oxidising agent—*i.e.*, it is eager to combine with hydrogen, and is capable of decomposing water, sulphuretted hydrogen, &c., under favourable circumstances (*e.g.*, sunlight), with liberation of oxygen, sulphur, &c. This property is made use of in the preparation of hydrobromic acid, which cannot be obtained pure by distilling a bromide with sulphuric acid (for reason above seen). By passing sulphuretted hydrogen through bromine mixed with water, a colourless solution of hydrobromic acid is obtained, and sulphur separates, thus:

$$Br_2 + SH_2 = 2HBr + S.$$

This solution always contains some sulphuric acid, owing to a secondary reaction of the bromine upon water, in the presence of nascent sulphur:

$$3Br_2 + 4OH_2 + S = 6HBr + H_2SO_4,$$

from which the hydrobromic acid is separated by distillation.

It will be inferred from this that the decomposition of water by bromine would be assisted very much by the presence of deöxidising bodies, such as phosphorus, metallic hypophosphites, sulphites, hyposulphites.

Hydrobromic acid can likewise be prepared by distilling an alkaline bromide with phosphoric acids, HPO_3, or H_3PO_4.

To detect a chloride in the presence of a bromide, the solution is acidulated with dilute nitric acid and an *excess* of silver nitrate is added. After shaking the precipitate is washed by decantation, and then agitated with very dilute ammonia, so as not to dissolve all the

* If test-tubes be worked with, then a little ammonium nitrate (10 grms.) or chloride, with its own weight of water, will form a good enough freezing mixture and can be contained in a small dish.

precipitate. The ammonia extract is filtered off and acidulated with nitric acid when a white precipitate is obtained.

A convenient plan of preparing pure HBr is to decompose PBr_3 (phosphorus bromide) by water thus:

$$PBr_3 + 3OH_2 = H_3PO_3 + 3HBr.$$

Water is "dropped" into PBr_3, contained in a small retort or distilling flask, from a dropping funnel and the escaping HBr led into cold water.

The phosphorous bromide is prepared by the action of bromine upon phosphorus in a CS_2 solution. The CS_2 is distilled off on a water bath, and the residual PBr_3 distilled by itself.

PBr_3 can also be made from amorphous phosphorus treated with bromine as above. The HBr can be collected by downwards displacement as with HCl.

Similar experiments should be made with it as with HCl (*ante*).

BROMIC ACID, $HBrO_3$.—Is obtained in combination with potassium by adding bromine to a moderately concentrated solution of *potassium hydrate*. Potassium bromate crystallises out from the slightly yellowish coloured liquid and is purified from potassium bromide by washing with water and recrystallisation. The reaction takes place according to the equation:

$$3Br_2 + 6KHO = 5KBr + KBrO_3 + 3OH_2.$$

The free acid is obtained by decomposing barium bromate with dilute sulphuric acid.

It is doubtful whether bromates occur in Nature. They are also seldom employed or made.

DRY REACTIONS.

All bromates are decomposed by heat. Some, *e.g.*, the alkaline bromates, fuse and evolve oxygen, leaving a bromide; others, such as zinc and magnesium bromates, leave an oxide and give off oxygen and bromine; others, again, leave an oxide and a bromide, *e.g.*, lead and cupric bromates. When mixed with readily oxidisable substances, such as carbon, sulphur, &c., bromates deflagrate like chlorates.

REACTIONS IN SOLUTION.

Employ a solution of potassium bromate, $KBrO_3$.

This is made by dropping bromine into hot strong KHO solution. The bromate is formed by a similar reaction to the chlorate and crystallises out very easily.

All bromates are soluble in water; silver and mercurious bromates least so.

Dilute sulphuric, nitric, or phosphoric acids liberate from its salts bromic acid, which, however, exhibits great instability and breaks up into bromine, oxygen, and water very rapidly.

Bromates are readily decomposed by deoxydising substances, such as sulphurous and phosphorous acids, sulphuretted hydrogen, &c., with formation of sulphuric and phosphoric acids, sulphur and water, and liberation of bromine. A mixture of potassium bromide and bromate, when acted upon by dilute acids, is decomposed into bromine and water, thus:—

$$5KBr + KBrO_3 + 6HCl = 3Br_2 + 3OH_2 + 6KCl.$$

The weak affinity of bromine for oxygen is, moreover, rendered apparent on boiling bromine with such powerful oxidising agents as nitric acid, potassium chlorate or manganate, which are without action upon it.

A bromate in the presence of a chlorate is readily distinguished by precipitation with $AgNO_3$; the white silver bromate, $AgBrO_3$, gives off bromine on being treated with HCl. The residue which bromates and chlorates leave on ignition may also be tested by any of the methods described under hydrochloric and hydrobromic acids.

HYDRIODIC ACID, HI.—Iodides (KI, NaI, MgI_2, CaI_2) occur in sea water, in the ashes of marine plants, in some mineral springs, and in Chili saltpetre and some borax deposits, from which bodies iodine is obtained by processes similar to those employed for the extraction of bromine from bromides.

Very little HI is obtained by acting on an iodide with H_2SO_4, owing to the ease with which HI becomes oxydised by the H_2SO_4.

DRY REACTIONS.

Most iodides undergo decomposition when heated by themselves, either with or without exclusion of air. Some few give off iodine, and leave the metals; others are partially decomposed, giving off iodine, and leaving an oxide of the metal. The alkaline iodides, also those of silver and a few others, can be heated to fusion, without undergoing any decomposition. Ignition with ammonium chloride converts iodides only partially into chlorides. On fusing cupric oxide in a bead of microcosmic salt, and introducing a little potassium iodide into the bead and heating in the inner blowpipe flame, the outer flame becomes of a fine emerald-green colour.

REACTIONS IN SOLUTION.

A solution of potassium iodide, KI, may be used.

All metallic iodides may be divided into—

1st. Iodides insoluble in water, such as AgI, Hg_2I_2, HgI_2, Cu_2I_2, (BiI_3, AuI_3, PtI_4), and PdI_2, and—

2nd. Iodides soluble in water, comprising all others. The iodides of the heavy metals are less soluble than the corresponding bromides or chlorides.

Some elements, the chlorides of which are well known, only form iodine compounds with great difficulty—*e.g.*, sulphur, carbon.

Soluble iodides may be examined in two ways—

1st. By precipitation or conversion of the soluble into insoluble iodides.

$AgNO_3$ gives a yellowish-white precipitate of silver iodide, AgI, insoluble in dilute nitric acid, almost insoluble in ammonium hydrate (partial distinction between HI and HCl), soluble in potassium cyanide or KI, or NaCl, or HCl solutions.*

$Hg_2(NO_3)_2$ gives a yellowish-green precipitate of mercurous iodide, Hg_2I_2, very slightly soluble in water, insoluble in dilute nitric acid, soluble in potassium iodide.

$HgCl_2$ gives a beautiful scarlet-red precipitate of mercuric iodide, HgI_2, little soluble in water, soluble in alcohol, and soluble also in excess either of mercuric chloride or of potassium iodide.

Lead acetate gives a bright yellow precipitate of lead iodide, PbI_2, dissolving, like the chloride, in hot water (120 parts), to a colourless solution from which it crystallises out, on cooling, in beautiful shining yellow scales; soluble in dilute nitric acid.

Cu_2SO_4 (cuprous sulphate), obtained by treating $CuSO_4$ with SO_2, or adding a sulphite or ferrous sulphate, or boiling the iodide with $CuSO_4$ and metallic copper, produces a dirty-white precipitate of cuprous iodide, Cu_2I_2, insoluble in water, sparingly soluble in HCl, soluble in ammonium salts and ammonium hydrate. *This precipitate is of particular interest, because chlorides and bromides cannot be precipitated in like manner, and because it serves frequently for removing iodine from solutions containing chlorides and bromides.*

2nd. By liberating iodine, and causing the iodine vapour to act upon starch paste. This may be effected in several ways.

On mixing a dilute solution of potassium iodide with a few drops of hydrochloric acid, and then adding a drop or two of a solution of potassium nitrite, iodine is instantly liberated, and may be detected by the yellowish-brown tint it imparts to the solution, or better still by allowing it to act upon a freshly prepared solution of starch, to which it imparts a fine blue colour. This is one of the most delicate tests. The reaction serves equally well for the detection of HNO_2 (which see) thus:

$$2KI + 2KNO_2 + 4HCl = I_2 + 4KCl + N_2O_2 + 2OH_2.$$

A solution containing free iodine may also be shaken up with a few drops of carbon disulphide, which dissolves the iodine, assuming

* AgI is very soluble in either the strong haloid acids or in the salts of haloids, especially so in lithium chloride and fluoride. $AgNO_3$ may be dropped into strong KI solution and the AgI formed observed to dissolve immediately. Water or nitric acid reprecipitates AgI. With the latter some $AgIO_3$ is liable to be formed.

a fine violet colour. Ether dissolves iodine, but the colour which is produced resembles ether coloured by bromine.

Bromine or chlorine (or what amounts to the same, ClNaO and HCl, or metallic peroxides or perchlorides, *e.g.*, BaO_2, PbO_2, MnO_2 and HCl, or Fe_2Cl_6 and HCl), liberate iodine from iodides. According to the quantity of iodide employed, the iodine separates either as a bluish-black powder, or it merely colours the solution brown.

The methods adopted for the extraction of iodine from metallic iodides are all based upon the expulsion of iodine by oxygen (or its equivalent of chlorine or bromine). Iodine is obtained by distilling an iodide with an oxidising agent and sulphuric acid, *e.g.*,—

$$2KI + MnO_2 + 2H_2SO_4 = I_2 + MnSO_4 + K_2SO_4 + 2OH_2, \text{ or}$$
$$6KI + K_2Cr_2O_7 + 7H_2SO_4 = 3I_2 + Cr_2(SO_4)_3 + 4K_2SO_4 + 7OH_2.$$

Concentrated acids, such as H_2SO_4, or HNO_3, decompose iodides with separation of bluish-black scales of iodine and evolution of SO_2 or lower oxides of nitrogen, thus:

$$2KI + 2H_2SO_4 = I_2 + K_2SO_4 + SO_2 + 2OH_2.$$
$$2KI + 4HNO_3 = I_2 + 2KNO_3 + N_2O_4 + 2OH_2.$$

On fusing an iodide with hydrogen potassium sulphate, $HKSO_4$, iodine is likewise liberated, thus:

$$2KI + 4KHSO_4 = 3K_2SO_4 + SO_2 + I_2 + 2OH_2.$$

On examining for traces of iodine in aqueous solutions by the action of chlorine, excess should be carefully avoided, as the iodine is oxidised by the chlorine to colourless iodic acid, which does not give the blue colour with starch, or the violet colour to the carbon disulphide solution. Previous to this a tri-chlorine of iodine, ICl_3, is very likely formed. The blue colour of iodide of starch is destroyed by various reducing agents, such as SO_2, SH_2, As_2O_3, $SnCl_2$, and Hg_2Cl_2. Alkalies also destroy the colour, but it reappears on acidification. The colour does not show so well in hot solutions.

The destruction of the blue colour of iodide of starch by various reducing agents is due to the decomposition of water by the iodine, with formation of HI, the oxygen being transferred to the reducing agent, thus:

$$H_2SO_3 \text{ (a dilute solution)} + I_2 + OH_2 = H_2SO_4 + 2HI.$$
$$SH_2 + I_2 = 2HI + S.$$
$$H_3AsO_3 + I_2 + OH_2 = 2HI + H_3AsO_4.$$

Hydriodic acid solution is usually prepared by acting upon iodine suspended in water (or dissolved in hydriodic acid), with a current of SH_2. Sulphur separates and is removed by filtration, and the solution of hydriodic acid concentrated by distillation. This solution absorbs oxygen from the air, water being formed and iodine liberated, which dissolves in the undecomposed hydriodic acid and imparts a brown colour to the liquid.

Gaseous HI is best obtained by the decomposition of PI_3 by water. PI_3 is made by dropping iodine crystals on to dry phosphorus, either *a* or *β*, preferably the latter, as it can be dried in an oven; PI_3 is formed on very gently warming. This may be made in a flask or test-tube fitted with cork and tube (see *ante*), and a dropping funnel containing water. An excess of phosphorus should be present. HI is a very heavy gas and fumes more strongly than HBr or HCl in moist air. The tube in which it is collected must be very thoroughly dried. Perform the same series of experiments with HI as with HCl.

The few insoluble iodides may be fused with alkaline carbonates, or in the case of AgI and PbI_2 decomposed by means of metallic zinc. The aqueous extract is examined for iodine, and the residue for the metal.

IODIC ACID, HIO_3.—Potassium iodate is obtained, like the corresponding chlorate and bromate, by dissolving iodine in hot potassium hydrate. The iodate crystallises out first, being much less soluble than KI. The free acid can be prepared by decomposing barium iodate with sulphuric acid, thus:

$$Ba(IO_3)_2 + H_2SO_4 = 2HIO_3 + BaSO_4.$$

Iodic acid is best obtained by the action of strong boiling nitric acid upon iodine, or by passing chlorine through iodine suspended in water or dissolved in an alkaline iodide. This product is not pure. In addition to HIO_3 there are some higher oxidation products and the anhydride I_2O_5.

Iodates are said to exist in sea water.

DRY REACTIONS.

All iodates are decomposed upon ignition, some breaking up into an iodide, with evolution of oxygen; others into metallic oxides, iodine and oxygen being expelled. When heated with charcoal they explode less violently than chlorates or bromates.

REACTIONS IN SOLUTION.

A solution of potassium iodate, KIO_3 is used.

Alkaline iodates alone are soluble in water.

$BaCl_2$ gives a white precipitate of barium iodate, nearly insoluble in water and difficultly soluble in dilute nitric acid.

$AgNO_3$ produces a white crystalline precipitate of silver iodate, sparingly soluble in water and in dilute nitric acid, readily soluble in ammonium hydrate (distinction from HI). On the addition of a reducing agent, *e.g.*, SO_2, to the clear ammoniacal solution of silver iodate, a yellowish precipitate of AgI is obtained, thus:

$$AgIO_3 + 3H_2SO_3 = AgI + 3H_2SO_4.$$

Potassium iodate is decomposed by SH_2, with formation of potassium iodide and sulphuric acid, and precipitation of sulphur; by H_2SO_3, with separation of iodine, which (by the decomposition of water) is converted into hydriodic acid.

An iodate and iodide act upon each other in the presence of weak acids (*e.g.*, acetic acid), with liberation of iodine. Traces of an iodate in potassium iodide can, therefore, be detected by means of the starch reaction.*

Iodates which give off iodine when they come in contact with various reducing agents, *e.g.*, SO_2,$Na_2S_2O_3$, $SnCl_2$, differ, however, in a marked manner from chlorates and bromates by remaining unacted upon by concentrated sulphuric acid, unless the action be assisted by deoxidising agents, such as ferrous salts, &c.

HYDROFLUORIC ACID, HF.—Fluorine minerals, as CaF_2, $Al_2F_6(NaF)_6$, yield HF by the action of strong acids (sulphuric, phosphoric). No compound of F and O alone is known, although many metallic oxides form with it oxyfluorides.

DRY REACTIONS.

Heated out of contact with the air, most fluorides melt but otherwise remain unchanged. Volatile fluorides can be distilled; but when heated in a moist atmosphere, or if water be added, they are decomposed into oxides (oxyfluorides) and hydrofluoric acid. The changes which fluorides undergo in the dry way are of two kinds.

1st. The fluoride gives off hydrofluoric acid gas, which corrodes glass.—By heating a fluoride containing water in a piece of combustion tubing, open at both ends, before the blowpipe, the glass around the fluoride is attacked. The experiment may be carried out also by mixing a little microcosmic salt with the fluoride.

By heating a mixture of a fluoride with hydrogen potassium sulphate, HF is disengaged, thus:

$$CaF_2 + 2KHSO_4 = CaSO_4 + K_2SO_4 + 2HF.$$

If the operation is done in a test-tube, the gas corrodes the upper part of the tube on account of its action upon the silica of the glass, with which it forms a gaseous compound, silicon fluoride, SiF_4, thus:

$$4HF + SiO_2 = SiF_4 + 2OH_2.$$

(See Fluorine.)

2nd. The fluoride is decomposed by hydrogen potassium sulphate in the presence of a borate, with formation of volatile boron fluoride, BF_3.—By heating a mixture† of powdered hydrogen potassium sul-

* Commercial KI almost invariably contains some iodate. Before using it should be ignited, melted, either alone or better with a little charcoal or sugar.

† 10 mol. of $KHSO_4$ (= 10 × 136).
3 mol. of CaF_2 (= 3 × 78).
1 mol. of $B_4O_7Na_2$ 202.

phate and fused borax with the finely powdered fluoride, on the loop of a platinum wire, in the clear flame of a Bunsen gas lamp, boron fluoride is disengaged, imparting a beautiful yellowish-green colour to the flame. But this is useless as indicating the presence of HF unless care is taken to distinguish between it and the colour given to the flame by the acid and borax alone.

REACTIONS IN SOLUTION.

Employ a solution of an alkaline fluoride.

Most metallic fluorides are solid; others, again, such as the fluorides of the metals whose higher oxides possess acid properties, form volatile, fuming, highly corrosive liquids, or are gaseous at the ordinary temperature. Non-metallic elements form gaseous or liquid fluorides.

Fluorides are either soluble in water and more or less crystalline, such as KF, NaF, NH_4F, AgF, SnF_2, Fe_2F_6, HgF_2, Al_2F_6, or insoluble or very sparingly soluble in water, and amorphous when obtained by precipitation, *e.g.*, CaF_2, BaF_2, PbF_2, ZnF_2, CuF_2.

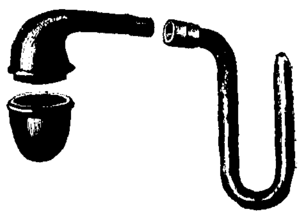


FIG. 23.

The reactions which a soluble fluoride gives by double decomposition with solutions of salts, whose metals form insoluble fluorides, are not very characteristic.

$BaCl_2$ produces a bulky white precipitate of barium fluoride, BaF_2, soluble in hydrochloric acid and in much ammonium chloride.

$CaCl_2$ (or $Ca(HO)_2$) gives a gelatinous translucent precipitate of calcium fluoride, CaF_2, which becomes more marked by the addition of ammonium hydrate. CaF_2 is slightly soluble in cold hydrochloric or nitric acid, more soluble in boiling hydrochloric acid, less soluble in acetic acid, insoluble in free hydrofluoric acid, soluble to some extent in ammonium chloride.

$AgNO_3$ produces no precipitate. (Distinction between HF and HCl.)

It is preferable to test for HF by the reactions based upon the formation of gaseous SiF_4 or BF_3.

All fluorides (soluble or insoluble) are decomposed on heating with concentrated sulphuric acid, with disengagement of HF, a metallic sulphate being left, thus:

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

The preparation of hydrofluoric acid is best performed by treating the fluoride with sulphuric acid in a small leaden cup heated over a water-bath (Fig. 23), and connected with a leaden U-tube, surrounded with ice, for the condensation of the acid.

Hydrofluoric acid gas is highly corrosive and should not be

inhaled. If it come in contact with silica (*e.g.*, in glass), SiF_4 is formed, and the glass becomes corroded or etched.

Its reaction upon glass may be shown also by covering a platinum crucible containing a little finely powdered fluoride and concentrated sulphuric acid with a piece of glass, *e.g.*, a watch glass. The vapour of the evolved hydrofluoric acid corrodes the glass. The action of the hydrofluoric acid becomes apparent when the glass is covered with a thin layer of melted wax, and some design scratched on the waxed side with a pointed instrument. The gas acts upon the unprotected portion of the glass. The design will be found etched more or less deeply into the glass, after the removal of the wax. Mere traces of a fluoride are thus detected, and as no other substance attacks glass similarly, the reaction is perfectly characteristic for hydrofluoric acid. It should be remembered, however, that the softer kinds of glass are liable to be corroded by the vapour of ordinary acids alone. In doubtful cases, therefore, it is preferable to employ a glass-bulb blown out of combustion glass, or else a plate of rock-crystal.

If the fluoride contains much silica, sulphuric acid disengages silicon fluoride instead of hydrofluoric acid, which does not attack glass; but when passed into water—best by letting the delivery-tube dip into a little mercury under the water to keep the tube opening clear—it is decomposed into hydrofluosilicic acid and into $Si(HO)_4$, thus:

$$3SiF_4 + 4OH_2 = Si(HO)_4 + 2(2HF,SiF_4).$$

This reaction is employed for detecting fluorine in silicates, or if applied to fluorides which are free from silica, some finely powdered quartz or glass is first mixed with the fluoride, before treating it with sulphuric acid.

The experiment may be performed in a glass flask or small stoneware bottle, provided with a wide delivery-tube, which dips under mercury contained in a small porcelain cup at the bottom of a beaker or glass cylinder. Care should be taken that the inside of the delivery tube remains perfectly dry when the receiving vessel is filled with water. A mixture of one part by weight of finely powdered fluorspar, and one by weight of fine sand is introduced into the glass or stoneware vessel. Seven to eight parts by weight of oil of vitrol are added, and the whole shaken gently together and heated upon a sand-bath. Each bubble of the evolved SiF_4, on passing through the water, is decomposed, with separation of gelatinous silica, which after a time fills the water in the form of a dense jelly. The silica is separated by straining through a cloth from the hydrofluosilicic acid, which may be returned to the glass cylinder, and a fresh quantity of SiF_4 passed through, till the acid solution has become sufficiently concentrated.

Silicates containing fluorides which are not decomposed by sulphuric acid, are fused with four parts of fusion mixture. The fused mass is extracted with water and filtered. The filtrate contains the

fluorine in the form of alkaline fluorides together with the alkaline silicates. On slightly acidulating with dilute hydrochloric acid to decompose the excess of alkaline carbonates, and then digesting with ammonium hydrate, $Si(HO)_4$, is precipitated, which can be filtered off, leaving the alkaline fluoride. On adding $Ca(HO)_2$ or $CaCl_2$, and digesting at a gentle heat, a gelatinous precipitate of CaF_2 is obtained, which is filtered off, dried, and examined. If phosphoric acid be present, the precipitate contains $Ca_3P_2O_8$, as well as CaF_2, which does not, however, interfere with the disengagement of hydrofluoric acid gas.

Insoluble fluorides, *e.g.*, CaF_2, are not completely decomposed by fusion with alkaline carbonates unless SiO_2 be present.

HYDROFLUOSILICIC ACID, $2HF,SiF_4$.—Obtained by passing silicon fluoride into water and separating the precipitated silica by filtration.

It forms salts, called silicofluorides, or fluosilicates, on acting upon metallic oxides, hydrates, or metals, such as Fe or Zn (these latter with evolution of hydrogen), of which the potassium and barium silicofluorides are insoluble.

DRY REACTIONS.

Silicofluorides are decomposed by heat into fluorides and silicon fluoride.

REACTIONS IN SOLUTION.

A solution of the acid may be employed.

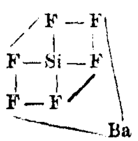
On evaporating a solution of hydrofluosilicic acid, it volatilises, and is decomposed into SiF_4 and $2HF$. The acid ought not, therefore, to be heated in a glass vessel.

A few silicofluorides, $2KF,SiF_4$, $2NaF,SiF_4$, BaF_2,SiF_4,* are difficultly soluble in water, and are quite insoluble in alcohol. Most other metallic silicofluorides are readily soluble in water.

$BaCl_2$ precipitates translucent crystalline barium silicofluoride, BaF_2,SiF_4, which falls out very readily. The precipitation is complete on the addition of an equal volume of alcohol. Strontium is not precipitated. (Distinction between barium and strontium.)

KCl gives a translucent gelatinous precipitate of potassium silicofluoride, $2KF,SiF_4$.

* The formulæ of these double fluorides may be written on the same type as the double chlorides, although, as yet, any absolute proof of "ring" or cycloid grouping is wanting.



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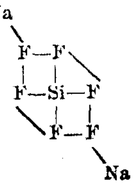


NH_4OH separates $Si(HO)_4$ and forms NH_4F.

On heating a metallic silicofluoride with concentrated sulphuric acid, hydrofluoric acid is evolved.

PHOSPHORIC ACID, H_3PO_4.—This acid is never met with in the free state in Nature, but in combination with bases, such as CaO, MgO, Al_2O_3, FeO, Fe_2O_3, PbO, as bone-ash, sombrerite, coprolite, apatite, wagnerite, wavellite, vivianite, pyromorphite, &c.

DRY REACTIONS.

Most anhydrous metallic phosphates, when mixed with dry sodium carbonate and carbon, or black flux, or heated together with metallic sodium or magnesium in a narrow ignition-tube, yield phosphides of these metals recognisable by the smell of PH_3, which is given off when they are moistened with water.

Normal phosphates of fixed bases are not decomposed upon ignition. Mono- and di-hydrogen normal phosphates lose water, and are converted into pyro- and metaphosphates, thus:

$$(1)\ 2Na_2HPO_4 = \underset{\text{Sodium pyrophosphate}}{Na_4P_2O_7} + OH_2.$$

$$(2)\ NaH_2PO_4 = \underset{\text{Sodium metaphosphate}}{NaPO_3} + OH_2.$$

Fusion with caustic or carbonated alkalies converts pyro- and metaphosphates into normal or orthophosphates. Boiling with acids also effects this conversion.

Alkaline earthy phosphates are only partially decomposed by fusion with alkaline carbonates; most others, *e.g.*, magnesium, ferric, zinc, nickel, manganous, cupric phosphates are completely decomposed. The residue contains trisodium and tripotassium phosphates. $Al_2P_2O_8$ can only be decomposed by fusion with silica or sodium silicate (water glass) and fusion mixture,* being converted into sodium aluminium silicate and trisodium phosphate. (Comp. ALUMINIUM COMPOUNDS.)

REACTIONS IN SOLUTION.

Employ a solution of hydrogen disodium phosphate, HNa_2PO_4.

Phosphates may be divided into—

1st. Phosphates which are soluble in water, comprising the alkaline phosphates only; their solutions react alkaline; and

2nd. Phosphates which are insoluble in water, but soluble in mineral acids (some also in acetic acid), comprising all other metallic phosphates.

* One part of SiO_2, together with six parts of fusion mixture.

The following are some of the more important reactions by double decomposition :

$BaCl_2$ yields a white precipitate of hydrogen barium phosphate, $BaHPO_4$, difficultly soluble in ammonium chloride, soluble in nitric or hydrochloric acid.

$CaCl_2$ or $CaSO_4$ produces a white precipitate of calcium phosphate, $Ca_3P_2O_8$, readily soluble in mineral acids; soluble in acetic acid, when freshly precipitated; slightly soluble in ammonium chloride.

In dilute solutions of phosphates, Na_2HPO_4, for instance, calcium chloride sometimes fails to produce a precipitate. This may be due to the slight decomposition of calcium chloride in solution in water into calcium oxychloride and HCl which retains the calcium phosphate in solution; or to the formation of an acid calcium phosphate, $CaHPO_4$. Addition of ammonia brings down the precipitate $Ca_3P_2O_8$ in all cases.

$MgSO_4$ (or better still $MgCl_2$) in the presence of ammonium chloride and ammonium hydrate produces a white crystalline, quickly subsiding precipitate of ammonium magnesium phosphate, $NH_4MgPO_4 + 6\ Aq$, insoluble in ammonium hydrate, readily soluble in acids, even acetic acid. A dilute solution of a phosphate is only precipitated after some time. The precipitation is promoted by stirring and allowing the liquid to stand in a warm place, when the precipitate is seen to adhere, in the form of white streaks to those parts of the glass vessel which have been touched by the glass rod. Arsenic acid gives a similar precipitate.

$AgNO_3$ gives a light yellow precipitate of silver phosphate, Ag_3PO_4, soluble in ammonium hydrate and in nitric acid.

Lead acetate produces a white precipitate of lead phosphate, $Pb_3P_2O_8$, readily soluble in nitric acid, almost insoluble in acetic acid, as well as ammonium hydrate. If the precipitate is fused before the blowpipe on charcoal, the bead appears crystalline on cooling; no reduction to the metallic state takes place.

Fe_2Cl_6 gives a yellowish-white gelatinous precipitate of ferric phosphate, $Fe_2P_2O_8$, soluble in hydrochloric acid. The precipitate is somewhat soluble in excess of ferric chloride.

When phosphoric acid has to be removed from a phosphate dissolved in hydrochloric acid, *e.g.*, from the alkaline earthy phosphate, $Ca_3P_2O_8$, the free acid is nearly neutralised and then sodium acetate is added, which by double decomposition with the free hydrochloric acid, forms sodium chloride and free acetic acid, in which the precipitate, produced by a slight excess of ferric chloride, is insoluble. The mixture is heated nearly to boiling; a reddish-brown precipitate is obtained, which contains the whole of the phosphoric acid, together with some basic ferric acetate. It must be filtered hot, and washed with hot water; the filtrate contains the alkaline earthy bases as chlorides.

Small quantities of phosphoric acid, in the presence of large amounts of a ferric salt, such as are met with in solutions of iron ores, of pig iron, steel, &c., are best removed by first reducing the ferric to ferrous salt by boiling with *sulphurous acid*, nearly neutral-

ising with sodium carbonate, and lastly adding sodium acetate and a few drops of ferric chloride (or by reoxidising a small portion of the ferrous salt by the addition of a little chlorine water, or a drop or two of bromine water). The phosphoric acid is precipitated by warming. Loss arising from the solvent action of ferric acetate is avoided, as ferrous acetate does not dissolve ferric phosphate.

H_3AsO_4 exhibits with ferric chloride a similar reaction, and has therefore to be separated from an acid solution, by reduction with sulphurous acid and precipitation by a current of SH_2 gas.

Small traces of phosphorus (phosphoric acid), usually found in soils, iron ores, in pig iron, steel, sheet copper, &c., may also be precipitated after dissolving the ore or metal in hydrochloric and nitric acids, whereby the phosphorus is converted into H_3PO_4, and after driving off the excess of acids by evaporation and taking up the residue with concentrated nitric acid, by adding a solution of ammonium molybdate and concentrated nitric acid; the silicic acid is separated by evaporation to dryness; and arsenic acid, if present, should be first removed by sulphuretted hydrogen. On digesting the solution at a gentle heat (60° C.) for some time (hours if necessary), a bright yellow precipitate of ammonium phospho-molybdate is obtained.

The constitution of this precipitate is somewhat complicated; it contains molybdic acid, ammonia, and phosphoric acid * (about 3 per cent.). By washing the yellow precipitate with a solution of ammonium molybdate, and lastly with a solution of ammonium nitrate, and then dissolving it in ammonium hydrate, filtering, and adding NH_4Cl, NH_4OH and $MgSO_4$, the phosphoric acid is obtained as NH_4MgPO_4.

White of egg (albumen) is not coagulated by tribasic phosphoric acid, nor by a solution of an orthophosphate acidulated with acetic acid.

PYROPHOSPHORIC ACID, $H_4P_2O_7$.—Pyrophosphates are obtained by heating monhydric phosphates. They are of little importance, however, since they are not usually met with in natural compounds, and as they are speedily converted by the action of acids and alkalies into tribasic phosphates.

REACTIONS IN SOLUTION.

Employ a solution of sodium pyrophosphate, $Na_4P_2O_7$.

Alkaline pyrophosphates are soluble in water.

All others are insoluble in water, but soluble in dilute acids.

The presence of a soluble pyrophosphate is indicated on adding $AgNO_3$, which gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$, soluble in nitric acid or ammonium hydrate.

Albumen is not coagulated by the free acid, nor by an acetic acid solution of a pyrophosphate.

$(NH_4)_2MoO_4$ (ammonium molybdate) does not give a precipitate

* MoO_3, 90·7 p.c.; P_2O_5, 3·1 p.c.; $(NH_4)_2O$, 3·6 p.c.; and OH_2, 2·6 p.c.

until by the action of mineral acids the pyrophosphate has been converted into a normal phosphate.

METAPHOSPHORIC ACID, HPO_3, is distinguished from the tetra- and tribasic acid as follows:

Albumen gives an abundant white precipitate with the free acid, and with soluble metaphosphates on the addition of acetic acid.

Magnesia mixture fails to precipitate soluble metaphosphates.

$AgNO_3$ produces a white precipitate of silver metaphosphate.

In the ordinary course of analysis both pyro- and metaphosphates are converted into normal phosphates, and their tetrabasic and monobasic nature is lost sight of. They can, therefore, only be detected by special experiments.

PHOSPHOROUS ACID, H_3PO_3 (dibasic).—Phosphorous anhydride, P_2O_3, is obtained by the slow oxidation of phosphorus on exposure to dry air at the ordinary temperature. By combining with water it forms a very weak acid.

DRY REACTIONS.

Heated by themselves on platinum foil, phosphites are decomposed, burning with a bright flame. Heated in a retort they evolve hydrogen, mixed towards the end of the decomposition with PH_3, and are converted into phosphates.

REACTIONS IN SOLUTION.

A solution of hydrogen sodium phosphite, HNa_2PO_3, may be employed.

Alkaline phosphites are soluble in water.

All other phosphites are, for the most part, difficultly soluble or insoluble in water, but soluble in acetic acid (lead phosphite excepted). Phosphites (as well as hypophosphites) are of interest, mainly on account of the powerful reducing action which they exert upon salts of various metallic oxides, capable of forming lower oxides, or of being reduced to the metallic state, as well as upon the lower oxides, &c., of metalloids, *e.g.*, SO_2.

$AgNO_3$ is reduced thereby to metallic silver, especially in the presence of ammonia and on the application of a gentle heat.

$HgCl_2$ and $Hg_2(NO_3)_2$, are reduced to Hg_2Cl_2 and metallic mercury.

SO_2 forms a phosphite with liberation of sulphur and evolution of SH_2.

If a phosphite be mixed with zinc and dilute acid, a mixture of hydrogen and PH_3 is evolved which fumes in the air and burns with an emerald-green colour. From a solution of silver nitrate PAg_3 and metallic silver may be precipitated by passing the gases through.

The difficultly soluble phosphites of Ba, Ca, Pb, &c., are obtained by double decomposition, the latter salt being insoluble in acetic acid.

HYPOPHOSPHOROUS ACID, $H.H_2PO_2$ (monobasic).—Obtained by the action of alkalies or hydrates of the alkaline earthy bases upon *a*-phosphorus and water.

$$P_4 + 3OH_2 + 3KHO = 3(KH_2PO_2) + PH_3.$$

DRY REACTIONS.

Hypophosphites are decomposed upon ignition into pyrophosphates and PH_3.

$$4KH_2PO_2 = K_4P_2O_7 + 2PH_3 + OH_2.$$

REACTIONS IN SOLUTION.

A solution of potassium hypophosphite may be employed.

All hypophosphites are soluble in water. They constitute even more powerful reducing agents than the phosphites.

Nitric acid or chlorine water changes them into phosphates.

H_2SO_4 is reduced to H_2SO_3, partly even to sulphur.

$CuSO_4$ is reduced to metallic copper (cupric hydride ?).

$HgCl_2$ is reduced to Hg_2Cl_2, and then to mercury.

$AuCl_3$ and $AgNO_3$ yield the metals.

$Zn + H_2SO_4$ (nascent hydrogen) yield H_2 and PH_3.

In the ordinary course of analysis, both phosphorous and hypophosphorous acids are converted into phosphoric acid, and they must therefore be identified by the special reactions just described.

Their soluble salts will act as photographic developers but are inconvenient substances to obtain.

SILICIC ACID (H_4SiO_4) (?).—Silicic anhydride or silica, SiO_2, occurs in Nature both in a crystalline and amorphous condition, either in the free or combined state. Quartz and rock crystal are composed of almost pure crystalline silica. Opal, hyalite, and some other minerals consist of amorphous silica, and are probably derived from silicon hydrate by a process of slow dehydration. Other silicious bodies, such as chalcedony, agate, flint, are principally composed of amorphous silica, or of a mixture of the two.

The compounds of silica with bases, especially with OK_2, ONa_2, CaO, MgO, Al_2O_3, FeO, MnO, are exceedingly numerous, and vary to a very great extent in their constitution and properties.

DRY REACTIONS.

Both varieties of silica are characterised by their infusibility when heated by themselves before the blowpipe, or in a bead of microcosmic salt. Pure silica fuses with sodium carbonate to a clear glass, which, if sufficient silica has been used, remains transparent on cooling. Silicates rich in silica behave like pure silica. If a fragment of a silicate is heated with microcosmic salt, its base or bases are dissolved, while the silica is seen to float about in the liquid

phosphate bead as a silica skeleton. Silicates containing coloured oxides give rise to opalescent beads in which the SiO_2 can be distinguished only with difficulty.

When silica, or a silicate rich in silica, is heated on platinum wire before the blowpipe with sodium carbonate, the SiO_2 displaces the CO_2, and forms a clear glass of sodium silicate. The alkaline carbonate should not be employed in excess. Calcium and magnesium silicates do not dissolve to a clear bead as a rule.

Beyond identifying silica and obtaining a general knowledge of the nature of any silicate under examination, respecting its fusibility, state of hydration, &c., the blowpipe reactions fail to supply distinguishing tests regarding the chemical composition of these bodies, since a very large number of silicates differ from each other merely in the relative proportions of their component metallic elements.

REACTIONS IN SOLUTION.

Silicates may be divided into—

1. Silicates which are soluble in water, include only potassium and sodium silicates; and
2. Silicates insoluble in water, including all others.

These latter silicates are either soluble in concentrated hydrochloric or sulphuric acid, or partly soluble and partly insoluble, or lastly insoluble in these acids.

All insoluble silicates are attacked by hydrofluoric acid, with disengagement of silicon fluoride, or by fusion mixture (or caustic baryta) at a high temperature.

By treating an aqueous solution of sodium silicate, Na_2SiO_3, with dilute hydrochloric acid, it is decomposed into NaCl and H_4SiO_4. The latter remains either dissolved in the acid, or is partially separated as a flaky or gelatinous mass. On evaporating in a porcelain dish over a water-bath, the gelatinous mass becomes firmer, and can be broken up, by means of a glass rod, into lumps, which speedily lose their water, leaving anhydrous silica. The dried mass is treated with a little concentrated hydrochloric acid and hot water, when NaCl is dissolved out (together with small quantities of Al and Fe—impurities in the sodium silicate), and the silica remains insoluble.

Ammonium chloride or carbonate precipitates H_4SiO_4 from a solution of sodium silicate. Salts of most of the heavy metals, as well as of the alkaline earthy metals, form by double decomposition with a soluble silicate, white or yellowish-white silicates, soluble in dilute hydrochloric or nitric acid, which, however, possess no characteristic properties. It is, therefore, necessary to remove the silica in order to detect bases, by evaporating to dryness with hydrochloric acid. On digesting the dry mass with a little hydrochloric acid, the metallic oxides are dissolved, and can be separated by filtration from the silica. SiO_2, like P_2O_5, is detected whilst testing for bases.

Most natural and artificial silicates are insoluble in water. Many, e.g., zeolites, as well as certain artificial silicates, such as slags from

blast furnaces, &c., are decomposed on digesting the finely powdered silicate with concentrated hydrochloric acid.

Silicates, such as *kaolin* and *clays*, *which are not attacked by* hydrochloric acid, can frequently be decomposed, either partially or wholly, by *hot concentrated sulphuric acid diluted with about one-third* of its weight of water: many natural silicates yield more or less silica, on treatment with hydrochloric acid, which silica may be taken to represent the soluble silica or the decomposable silicates, leaving the greater portion of the mineral behind in its original condition.

Silica, or silicates insoluble in acids, forming by far the greater number, are *readily attacked by gaseous hydrofluoric acid*, or by fluorspar and H_2SO_4, gaseous SiF_4 being given off. This method may be resorted to when alkalies are present in a silicate, as, *e.g.*, in felspar. A little of the finely powdered silicate is moistened with strong ammonia, put into a platinum crucible or small platinum capsule, and exposed to the action of gaseous HF. This gas should be generated in a leaden or platinum vessel. The platinum crucible is to this end supported on a lead tripod in a small leaden basin, which can be closed with a lid of the same metal. A layer of fluorspar is put at the bottom of this vessel, mixed and covered with concentrated sulphuric acid. The leaden vessel after being covered is placed for a day or two in a warm place. The crucible is then taken out, and its contents cautiously evaporated by applying a gentle heat, as shown in Fig. 24, from the upper part of the crucible downward, till the whole of the ammonium fluoride has been driven off. The dry residue is dissolved in hydrochloric acid and tested for bases. A small residue is usually left, which is filtered off and treated once more in the same manner.

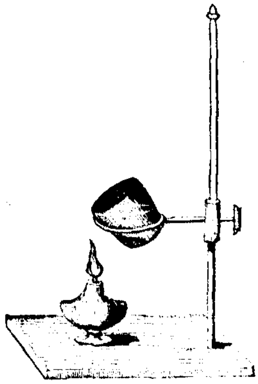


FIG. 24.

An expeditious way of detecting SiO_2 with certainty is to warm a little of the finely powdered mineral, mixed with fluorspar, with strong sulphuric acid in a piece of lead tube closed at one end, and bent almost into a U-form, with the open limb shorter than the other. On arranging this to dip only just below the surface of water in a small beaker, and applying heat to the closed limb containing the mixture, SiF_4 will be given off, and form gelatinous SiO_2 in contact with the water.

The same result may be obtained more expeditiously by treating the mineral in a platinum crucible with liquid hydrofluoric acid, and evaporating cautiously in a well-ventilated draught closet. The residue is dissolved in hydrochloric acid. Any insoluble part which may be left is separated by filtration and treated again with hydrofluoric acid. This treatment has generally to be repeated

several times, before the whole of the bases are obtained in a soluble condition.

Treatment with CaF_2 and concentrated H_2SO_4 is sometimes objectionable, on account of the formation of insoluble $CaSO_4.OH_2$.

A less cumbersome yet equally satisfactory method for decomposing silicates in order to detect the alkalies in them is the following:—Mix ·5 grm. of finely powdered silicate intimately with ·5 grm. of pure NH_4Cl, and then with 4 grms. of pure precipitated granular calcium carbonate,* and heat the mixture in a platinum crucible, first gently and by means of a small Bunsen flame till the ammonia is volatilised. Then apply a stronger heat, and lastly heat for half an hour over a good Bunsen lamp. The sintered mass consists now of caustic lime, disintegrated silicate (rendered soluble in acids), and alkaline chlorides soluble in water, besides $CaCl_2$. It is next slaked and repeatedly extracted with small quantities of hot water at a time. The liquid after filtration is free from silica and contains the alkali metals as chlorides. The lime in solution is removed by precipitation with ammonia and ammonium oxalate, and the filtrate evaporated to dryness and gently ignited, when the fixed alkali salts are left behind.

All silicates insoluble in water and acids may be decomposed by fusion with alkaline carbonates (fusion mixture). They are first ground up very finely in an agate mortar, then intimately mixed with three or four times their weight of fusion mixture and heated in a platinum crucible as long as any CO_2 is given off. This may be done over a good Bunsen gas lamp or by means of a gas blowpipe. (A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established by a preliminary examination of the silicious substance on charcoal.) The mass is at once treated with dilute hydrochloric acid and evaporated to dryness. The residue is treated with a little HCl, water is added, and the solution of the base filtered from the silica. The alkalies must be examined for in a separate portion by treatment with hydrofluoric acid.

Pure amorphous silica dissolves completely when boiled with an aqueous solution of fixed caustic or carbonated alkalies.

SiO_2 is separated from TiO_2 (titanic anhydride) by fusion with $HKSO_4$, and subsequent treatment with water; the SiO_2 remains undissolved. The TiO_2 is precipitated from the acidulated aqueous solution by long-continued boiling.

BORIC ACID, H_3BO_3 (Orthoboric Acid).—Is found in Nature both combined and in the free state.

DRY REACTIONS.

Most borates swell up when heated by themselves, and fuse into a transparent glass. The free acid forms scaly crystals,

* Prepared by precipitating a dilute solution of $CaCl_2$, at 70° C. with excess of ammonium carbonate, and washing the precipitate thoroughly with hot water by decantation.

possessing a pearly lustre and feeling peculiarly greasy to the touch.

When heated to 100° C. the crystals lose water and become converted into metaboric acid, HBO_2, and by further heating this acid fuses to a colourless transparent, glassy-looking mass of boric anhydride, B_2O_3, which can be kept in a fused condition without loss from volatilisation.

A mixture of $KHSO_4$ and a borate, heated on a platinum wire in the blowpipe flame, imparts a green colour to the flame, owing to the liberation of boric acid.

To detect small quantities of boric acid before the blowpipe, the borate is powdered and mixed with $KHSO_4$ and CaF_2.* The mixture is made into a stiff paste with a few drops of water, and cautiously introduced, on the loop of a platinum wire, into the inner blowpipe flame, when the outer flame acquires momentarily a yellowish-green tint, owing to the volatilisation of boric fluoride, BF_3. Phosphates, as well as copper salts, when moistened with sulphuric acid and heated in the outer flame, give likewise a green tint to the flame.

REACTIONS IN SOLUTIONS.

A solution of borax, $Na_2B_4O_7$, is used.

The alkaline borates are soluble in water, all others are difficultly soluble, but none are absolutely insoluble. All borates dissolve in acids and ammonium chloride.

The precipitates produced by double decomposition of a soluble alkaline borate with salts of the alkaline earths, or with lead, silver, mercurous, or ferrous salts, &c., are white or yellowish-white, and are readily soluble in acids and ammonium chloride.

The free acid dissolves in water and alcohol, and its solutions impart to a Bunsen gas flame a fine green colour. An alcoholic solution inflamed in a porcelain dish, or, better still, in a test tube, gives the same characteristic flame, and the colour becomes all the more perceptible when the burning alcohol is stirred with a glass rod. The B_2O_3 is volatile along with the alcohol, which is not the case with other substances, as Cu or Ba salts. A borate mixed with strong sulphuric acid shows the same reaction, but it is preferable to make a paste of the substance with strong H_2SO_4, and to bring a small quantity of this on a platinum wire near to the lower part of a non-luminous flame. The boric acid is shown by the green flame.

A green flame (of a somewhat greenish-blue tint, however) is obtained also by heating many metallic chlorides with alcohol and concentrated sulphuric acid (owing to the formation of ethylic chloride, C_2H_5Cl), also by passing hydrochloric acid gas into the flame of burning alcohol.

If a borate cannot be decomposed by sulphuric acid, it is fused

* Three to four parts of the flux (consisting of one part of powdered CaF_2 and four and a half to five parts of $KHSO_4$).

with potassium hydrate, and the fused mass may be extracted with alcohol, or it may be tested as above.

An aqueous solution of boric acid cannot be evaporated without loss of acid from volatilisation.

An alcoholic solution of boric acid colours turmeric paper reddish-brown, especially on drying the strips of paper in a warm place (a water-oven). This colour becomes more intense in the presence of hydrochloric or sulphuric acid (even in the presence of nitric or tartaric acid). The colour produced by heating turmeric paper with hydrochloric acid is blackish-brown, and must not be confounded with the colour produced by boric acid. The dried paper acquires a green or a blackish tint when touched with alkalies, as soda.

Hydrofluoric acid (or H_2SO_4 and CaF_2) decomposes all borates, with formation of volatile boric fluoride, thus:

$$Na_2B_4O_7 + 6CaF_2 + 7H_2SO_4 = 6CaSO_4 + Na_2SO_4 + 4BF_3 + 7OH_2,$$

and if the gaseous boric fluoride be passed into water, it forms hydrofluoboric acid, thus:

$$4BF_3 + 3OH_2 = \underset{\text{Hydrofluoboric acid}}{3(BF_3,HF)} + H_3BO_3$$

This acid combines with bases, forming borofluorides or fluoborates, thus:

$$BF_3,HF + KHO = BF_3,KF + OH_2.$$

ORGANIC ACIDS.

HYDROCYANIC ACID (Prussic acid), HCy.—This acid* consists of hydrogen and the compound radical cyanogen, Cy, molecule $\begin{matrix}CN\\CN\end{matrix}$. It forms salts called cyanides, which are analogous in their chemical constitution to chlorides, bromides, &c. Cyanogen cannot be obtained technically by the direct combination of carbon and nitrogen, although it is formed in the electric arc, but an alkaline cyanide results from the action of caustic or carbonated alkalies upon nitrogenous organic bodies, such as fibrin, albumen, and gelatin at a high temperature. Commercial cyanide of potassium contains some cyanate, and generally a large quantity of carbonate.

When organic substances containing nitrogen are heated with

* The compounds which the radicals cyanogen, ferro- and ferri-cyanogen, &c., are capable of forming will be treated somewhat more fully, since a thorough understanding of the various reactions is necessary in order to analyse cyanogen compounds successfully.

sodium or potassium, and some other metals, as Mg or Fe, the two elements, C and N, seem to be simultaneously liberated and then combine with the alkali (or other metal) to form a compound which is very stable at a high temperature. In order that the whole of the nitrogen may be resolved into this form, it is necessary for any oxygen present to be fully taken up, either as water by excess of hydrogen, or as CO, carbon monoxide, by carbon. Alkaline cyanides are formed in the iron blast furnace.

DRY REACTIONS.

KCy and NaCy are not decomposed upon ignition in close vessels, as may be inferred from their mode of manufacture; but when heated with free access of air, they are converted into cyanates. The same change takes place, only more speedily, when potassium cyanide is heated with less energetic oxidising agents, such as MnO_2, PbO_2, PbO, CuO, SnO_2, &c., when the metal or a lower oxide is left. *Heated in the presence of metallic sulphides, it is converted into* potassium sulphocyanate, KSCy. Potassium cyanide is on this account a most valuable deoxidising and desulphurising agent, and is employed in blowpipe reactions whenever a metallic oxide (or sulphide) has to be reduced to the metallic state. Cyanides of the heavy metals undergo decomposition upon ignition; some (*e.g.*, the cyanides of the noble metals) break up into metal and cyanogen gas; others into the metal, carbon and nitrogen (*e.g.*, the cyanides of iron); others again (such as AgCy, $HgCy_2$, $CuCy_2$, $ZnCy_2$) yield cyanogen gas, metallic silver, mercury, &c., and paracyanogen—a brownish-black substance, which is polymeric with cyanogen, usually expressed by the symbol Cy_n.

This deportment of solid cyanides furnishes ready means of preparing cyanogen gas, either by igniting dry $HgCy_2$, or AgCy: or by heating two parts of dry yellow prussiate of potash, or potassium ferrocyanide, K_4FeCy_6, with three parts by weight of dry $HgCl_2$.

CYANOGEN,* $\left\{\begin{array}{l}CN\\CN\end{array}\right.$, melting point −34·4° C., boiling point, 20·7° C.; specific gravity gas 1·799; liquid = ·866.—It is a colour-

* Cyanogen gas should on no account be prepared unless for some special purpose, and with every precaution against breathing the gas, owing to its fearfully poisonous nature. Cyanogen and its compounds with the alkali metals are extremely stable bodies at a high temperature. Great chemical stability is thought to be associated with or to depend upon a more or less symmetrical structure. That of cyanogen may perhaps be represented as $\begin{array}{l}C\equiv N\\|\\C\equiv N\end{array}$ although an isomeric form is possible $\begin{array}{lcl}N & = & C\\| & & \|\\N & = & C\end{array}$ and even $\begin{array}{lcl}C & \equiv & N\\| & & \|\\C & \equiv & N\end{array}$ which would be a ring or closed chain formula.

A cyanide might then be $\begin{array}{l}C\equiv N—K\\|\\C\equiv N—K\end{array}$ or $\begin{array}{lcl}N & = & C—K\\| & & |\\N & = & C—K\end{array}$ which is less in keeping with experiment. The cyanogen molecule contains, undoubtedly, "labile" elements.

less gas of peculiar odour, burning with a beautiful purple or peach-blossom coloured flame, and yielding CO_2 and N. The gas is nearly twice as heavy as air, and since water dissolves about four times its own volume it must be collected over mercury, or by downward displacement. In $CHCl_3$ or CCl_4 it is much more soluble. An aqueous solution decomposes spontaneously into a variety of products.* It is one of the few gases which condense to a liquid at a moderate pressure (3·6 atmospheres).

Cyanogen compounds when ignited in a tube with excess of soda-lime, give up the whole of their nitrogen as ammonia.

Reactions.—To test a gas for cyanogen it should be shaken up with caustic potash which absorbs the cyanogen, forming cyanide and cyanate of potassium, the solution of which may be tested as usual.

It is also absorbed by yellow ammonium sulphide forming sulpho-cyanate of ammonium, which is easily identified by the dark-red colour it gives with ferric salts.

REACTIONS IN SOLUTION.

The cyanides of the alkali metals and alkaline earthy metals are soluble in water, the former readily, the latter with difficulty. The cyanides of the heavy metals are insoluble in water, with the exception of $HgCy_2$; but are for the most part soluble in a solution of potassium cyanide, forming soluble double cyanides, which are frequently crystalline, and which upon ignition are decomposed like single cyanides, *i.e.*, *the cyanide of the heavy metals breaks up into* metal and cyanogen, or metal, carbon (carbide ?) and nitrogen, whilst the alkaline cyanide is not decomposed, and can be dissolved out from the residue.

The following is a list of some of the more important single cyanides, *i.e.*, cyanides which contain only one metal:

Potassium	cyanide,	soluble in water . .	KCy.
Sodium	,,	,, ,, . .	NaCy.
Barium	,,	difficultly soluble in water	$BaCy_2$.
Silver	,,	insoluble in water . .	AgCy.
Zinc	,,	,, ,, . .	$ZnCy_2$.
Cadmium	,,	,, ,, . .	$CdCy_2$.
Nickel	,,	,, ,, . .	$NiCy_2$.
Cobaltous	,,	,, ,, . .	$CoCy_2$.
Cuprous	,,	,, ,, . .	Cu_2Cy_2.
Mercuric	,,	soluble in water . .	$HgCy_2$.

Some of these single cyanides are readily decomposed by acids, with evolution of hydrocyanic acid; others are more stable.

* It *should* form ammonium oxalate exclusively from the following reactions:

$$\text{(I)}\ (NH_4)_2C_2O_4 - 4H_2O = C_2N_2;$$
$$\text{(II)}\ C_2N_2 + 4H_2O = (NH_4)_2C_2O_4.$$

The former can be carried out with the aid of P_2O_5 but the second is somewhat difficult to manage quantitatively.

Double cyanides contain, generally, a cyanide of an alkali metal, K or Na, and another cyanide as $Zn(CN)_2$ or $Cd(CN)_2$, &c. They seem to resemble to some extent some double chlorides. Most, if not all the insoluble cyanides are soluble in an excess of an alkaline cyanide. (See AgCy.)

The action of dilute acids upon double cyanides shows clearly the existence of two distinct classes of double cyanides—viz.:

1st. *Double cyanides which are readily decomposable, giving off* hydrocyanic acid when treated with dilute mineral acids. They possess an alkaline reaction. Their alkaline cyanide is decomposed by dilute mineral acids into HCN and a salt of the alkali metal, and into a cyanide of the heavy metal, which remains in combination with the liberated HCN, and this cyanide being insoluble is precipitated, or both cyanides are decomposed, and the whole of the HCy is liberated, *e.g.*:

$$(1)\ KAgCy_2 + HNO_3 = \underset{\text{Precipitated}}{AgCy} + HCy + KNO_3.$$

$$(2)\ K_2ZnCy_4 + 4HCl = ZnCl_2 + 2KCl + 4HCy.$$

2nd. Double cyanides which possess a neutral reaction and give off no hydrocyanic acid, when treated with dilute hydrochloric acid, the negative element of the acid forming a salt with the alkali metal, whilst the hydrogen or positive element, by uniting with the remaining elements, forms a new acid of a more complex nature, thus:

$$K_4FeCy_6 + 4HCl = \underset{\text{Hydroferrocyanic acid}}{H_4FeCy_6} + 4KCl.^*$$

$$K_6Fe_2Cy_{12} + 6HCl = \underset{\text{Hydroferricyanic acid}}{H_6Fe_2Cy_{12}} + 6KCl.$$

$$K_6Co_2Cy_{12} + 6HCl = \underset{\text{Hydrocobalticyanic acid}}{H_6Co_2Cy_{12}} + 6KCl.$$

The single, as well as easily decomposable double cyanides, which yield hydrocyanic acid, when treated with dilute mineral acids, are moreover remarkable for their highly poisonous character, whilst these latter—the double cyanides containing a very stable cyanogen radical, *e.g.*, ferrocyanogen, $FeCy_6$, cobalticyanogen, Co_2Cy_{12}—are not poisonous or not markedly so.

All these complex cyanogen compounds—both decomposable and non-decomposable—may be viewed as double cyanides.

The following list contains some of the more interesting double cyanides, *i.e.*, cyanides containing more than one metal; the easily

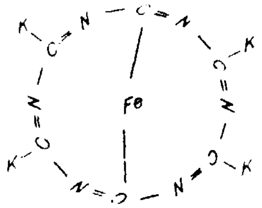
* In these salts (ferro- and ferri- and cobalti-cyanides) the constitution is very likely somewhat akin to that of benzene compounds, and is expressible as

decomposable class being indicated by a comma placed between the cyanogen and the metal:

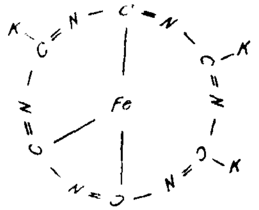
Potassium zinc cyanide	. . . .	K_2Zn,Cy_4.
,, cadmium cyanide	. . .	K_2Cd,Cy_4.
,, nickel ,,	. . . .	K_2Ni,Cy_4.
,, silver ,,	. . . .	KAg,Cy_2.
,, aurous ,,	. . . .	KAu',Cy_2.
,, auric tetracyanide	. . .	KAu''',Cy_4.

a closed chain, ring, or nucleus. Their much great stability, &c., certainly points to a different structure to that of single and decomposable double cyanides.

Potassium ferrocyanide might, for instance, be pictured as a cyanogen ring,

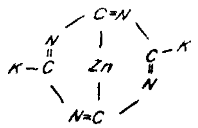


and when this is converted by oxidation into ferricyanide $K_3Fe(CN)_6$,

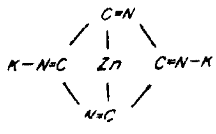


Of course the Fe or Co may be doing quite different work in these compounds to what they are doing in ordinary salts. There is no proof that it may not be tetravalent or hexavalent. Whether the iron is directly united to carbon or nitrogen or to the cyanogen molecule as a whole is all waiting for investigation to settle. In the meanwhile these views do no harm. In ferro and nickel carbonyls the metals can scarcely be otherwise than attached to carbon.

The easily decomposable double cyanides, as K_2ZnCy_4, might be expressed thus:



or a less probable form:



Potassium cuprous cyanide	$K'_2Cu'_2Cy_4$.
„ platinous „	$K_2Pt''Cy_4$.
„ *platinic* „	$K'_4Pt''''_2Cy_{12}$.
„ ferrous cyanide (potassium ferrocyanide, yellow prussiate) .	K_4FeCy_6.
„ ferricyanide, red prussiate . .	$K_6Fe_2Cy_{12}$.*
„ cobalticyanide	$K_6Co_2Cy_{12}$.*
„ *chromicyanide*	$K_6Cr_2Cy_{12}$.*
„ manganicyanide	$K_6Mn_2C_{12}$.*

If the different behaviour of these double cyanides with dilute acids and with ferroso-ferric salts be noticed, the easily decomposable double cyanides giving a precipitate of Prussian blue, whilst the others—the difficultly decomposable double cyanides—yield no hydrocyanic acid when treated with dilute acids, and produce (with the exception of the ferro- and ferri-cyanogen compounds) no precipitate of Prussian blue with ferroso-ferric salts and hydrochloric acid, it becomes evident that the complex groups of elements, ferrocyanogen, $FeCy_6$, ferricyanogen, Fe_2Cy_{12}, cobalticyanogen, Co_2Cy_{12}, &c., which behave, like cyanogen, as a group or complex, may likewise be viewed as compound radicals, if by this term is denoted a group of common and constant constituents found in a whole series of compounds, and capable of replacing multiplies of Cl, Br, &c., in constant atomic proportions.

It is possible to produce by double decomposition precipitates with soluble salts of almost all the heavy metals in which the potassium—or positive radical—is either entirely or partially exchanged for an equivalent quantity of a heavy metal, whilst the negative group of elements remains unaltered, thus :—

$$K_4FeCy_6 + CuSO_4 = K_2CuFeCy_6 + K_2SO_4, \text{ or}$$
$$K_4FeCy_6 + 2CuSO_4 = Cu_2FeCy_6 + 2K_2SO_4.$$

On the addition of an alkaline hydrate or carbonate, the whole of the heavy metal is removed as hydrate or carbonate, with formation of an alkaline ferrocyanide.

Easily decomposable soluble double cyanides give likewise precipitates with solutions of heavy metals, *e.g.* :

$$2KAgCy_2 + ZnSO_4 = \underset{\text{Precipitated}}{Zn_2Ag_2Cy_4} + SO_4K_2;$$

but there is no evidence to show whether these precipitates are real compounds or only mixtures of two insoluble cyanides ; nor is there any proof that alkaline hydrates reproduce the original double cyanide. *Dilute* sulphuric acid decomposes $ZnCy_2$ in the above precipitate, AgCy being left behind ; just as if no connection had existed between the two cyanides, or simply because the AgCN is so insoluble. Alkaline hydrates or carbonates are without action upon easily decomposable cyanides. A few are decomposed by sulphuretted

* These formulæ may be halved for simplicity, thus : K_3FeCy_6, &c.

hydrogen, *e.g.*, K_2CdCy_4, K_2HgCy_4, $KAgCy_2$, with precipitation of a metallic sulphide; in others, such as K_2MnCy_4, K_2NiCy_4, K_2ZnCy_4, and K_2CuCy_4, the metal is only partially precipitated.

It is evident from these changes that easily decomposable and difficultly decomposable double cyanides differ in stability, and this probably depends upon chemical structure as much as upon the individual nature of the metal they contain.

A solution of potassium cyanide, KCy, may be used for the wet reactions.

$AgNO_3$ gives a permanent white curdy precipitate* of silver cyanide, AgCy only, when more than one molecule of $AgNO_3$ has been added for every two molecules of KCy. The precipitate is insoluble in dilute nitric acid, soluble in ammonium hydrate, sodium thiosulphate, and potassium cyanide. AgCy resembles AgCl so very closely that special experiments are required to distinguish it from the latter, or to detect hydrocyanic acid in the presence of a chloride.

This may be done (1) by boiling with strong HNO_3, which dissolves AgCy but not AgCl; (2) by igniting a mixture of AgCl and AgCy, which has been entirely freed from silver nitrate by washing with hot water, when AgCy is decomposed into cyanogen, metallic silver, and paracyanogen. AgCl fuses without decomposition. On dissolving the residue in nitric acid and filtering, a precipitate of AgCl is obtained, on the addition of hydrochloric acid, or a soluble chloride, the silver of which must have been present originally as cyanide. (Distinction between HCl and HCy.)

Dilute mineral acids decompose potassium cyanide readily with evolution of HCy. On decomposing a small quantity of KCy by dilute sulphuric acid in a small porcelain dish and inverting another small dish containing a drop or two of yellow ammonium sulphide over it, the gaseous hydrocyanic acid, acting upon the ammonium sulphide, forms ammonium sulphocyanate, NH_4SCy, and NH_4HS, thus:

$$(NH_4)_2S_2 + HCy = NH_4SCy + NH_4HS.$$

which gives a characteristic blood-red coloration with Fe_2Cl_6.

This constitutes one of the most delicate reactions for free hydrocyanic acid, as well as for soluble or easily decomposable cyanides.

$CuSO_4$, to which a solution of SO_2 has been added, gives with KCy a white precipitate of cuprous cyanide, Cu_2Cy_2, soluble in potassium cyanide ($K_2Cu_2Cy_4$).

$Hg_2(NO_3)_2$ gives a grey precipitate of metallic mercury, whilst $HgCy_2$ remains in solution, thus:

$$Hg_2Cy_2 = Hg + HgCy_2.$$

Iron salts are among the most delicate reagents for hydrocyanic acid, or for soluble cyanides, on account of their tendency, especially

* $HgCy_2$ is not precipitated by silver nitrate.

in the presence of potassium hydrate, to form difficultly decomposable double cyanides (containing the compound acid radicals ferro- and ferri-cyanogen), which are of a characteristic blue colour. (Hence the name cyanogen, from κύανος, blue, γεννάω, I generate. The solution containing hydrocyanic acid, or a soluble cyanide, is first treated with a little potassium hydrate, then with a mixture of ferric chloride and ferrous sulphate, and heated. On the addition of dilute hydrochloric acid, in order to dissolve the ferrous and ferric hydrates precipitated by the potassium hydrate, a fine blue precipitate, or in the case of a mere trace of HCy, a green coloration only, of Prussian blue is obtained. The changes may be expressed by the equations—

$$(1)\ KHO + HCy = KCy + OH_2.$$
$$(2)\ FeSO_4 + 2KCy = FeCy_2{}^{*} + K_2SO_4.$$

$FeCy_2$, by combining with 4KCy, forms the soluble double cyanide K_4FeCy_6.

$$(3)\ 2Fe_2Cl_6 + 3K_4FeCy_6 = Fe_4(FeCy_6)_3 + 12KCl.$$

Free hydrocyanic acid dissolves mercuric oxide, with formation of mercuric cyanide, which is not precipitated by alkalies. $HgCy_2$ exhibits considerable stability compared with other cyanogen compounds. (Palladium cyanide is even more markedly stable.) A palladium salt will remove cyanogen from $Hg(CN)_2$. Boiling dilute H_2SO_4 does not decompose it. Strong HCl breaks it up into $HgCl_2$ and HCy. When SH_2 is passed through its aqueous solution it is decomposed into HgS and HCy.

The alkaline ferro- and ferri-cyanides are partially decomposed by warming with dilute sulphuric acid with evolution of hydrocyanic acid.

This furnishes a convenient method for preparing a solution of hydrocyanic acid. Ten parts by weight of K_4FeCy_6 (yellow prussiate of potash) are distilled in a flask or retort with 36 to 40 parts of dilute sulphuric acid (one of acid to six of water). The flask or retort is connected with a Liebig's condenser and double-necked receiver, from which any uncondensed gas can be carried under a Bunsen lamp, and burnt. Every joint should be made perfectly tight, and the condenser-tube should dip into the water placed in the receiver. The reaction takes place according to the equation:

$$2K_4FeCy_6 + 3H_2SO_4 = 6HCy + K_2Fe''FeCy_6 + 3K_2SO_4.$$

White residue
turning blue by exposure
to the atmosphere

That is, only half the cyanogen is given off as HCN.

* $FeCy_2$ is scarcely known in an isolated condition, as it forms in the presence of KCy potassium ferrocyanide, K_4FeCy_6, containing the compound cyanogen radical $FeCy_6$, which in its turn reacts upon the ferric salt.

A solution of HCy, in water or alcohol, when left to itself, undergoes spontaneous decomposition, with production of ammonium formate,* &c. HCN combines also with acids as HCl and some anhydrous chlorides. The compounds are mostly easily decomposed even by water. A mere trace of mineral acid retards this decomposition considerably.

Hydrocyanic acid is exceedingly poisonous. Small quantities of the gaseous acid, when inhaled, cause a peculiar sensation in the throat, and are followed by headache, giddiness, and other disagreeable symptoms. Great care must therefore be taken in operating with HCy, or with cyanogen compounds generally, and for the purposes of analysis small quantities only should be operated upon at a time.

HYDROFERROCYANIC ACID, H_4FeCy_6.—This acid is tetra-basic. The potassium salt is prepared on a manufacturing scale by introducing nitrogenous animal substances (horn shavings, &c.) and iron into fused crude potash. The fused mass is lixiviated with water and the salt allowed to crystallise out. It may also be prepared by decomposing Prussian blue with KHO or K_2CO_3, fused or strong boiling solutions, and separating the ferric hydrate by filtration, thus:

$$Fe_4(FeCy_6)_3 + 12KHO = 3K_4FeCy_6 + 2Fe_2(HO)_6.$$

Potassium ferrocyanide, $K_4FeCy_6 + 3Aq$, crystallises in large lemon-yellow crystals; hence its name, yellow prussiate of potash. Its positive element (potassium) can, by double decomposition, be replaced by other metals, either entirely or partially, and the property of cyanogen to form double cyanides is well illustrated by the reactions of the ferrocyanides. This will be seen from the following list of some of the more common of these:

$K_4FeCy_6 + 3Aq.$	$K_2CaFeCy_6 + 3Aq.$
$Na_4FeCy_6 + 6Aq.$	$Cu_2FeCy_6 + 4Aq.$
$(NH_4)_4FeCy_6 + 3Aq.$	$K_2CuFeCy_6 + 2Aq.$
$Ba_2FeCy_6 + 6Aq.$	$K_2FeFeCy_6.$
$K_2BaFeCy_6 + 3Aq.$	$NaK_3FeCy_6 + 3Aq.$
$Ca_2FeCy_6 + 12Aq.$	$NH_4K_3FeCy_6 + 3Aq.$

DRY REACTIONS.

K_4FeCy_6 fuses, when strongly ignited, and breaks up into nitrogen, potassium cyanide, and carbide of iron, or a mixture of carbon and iron, thus:

$$K_4FeCy_6 = 4KCy + 2C + Fe + N_2.$$

* Ammonium formate, NH_4O_2CH, when dehydrated gives

1st, $NH_4O_2CH - H_2O = NH_4OCH$ = formamide, and
2nd, $NH_4OCH - H_2O = NCH$ = formimide.

This is the reverse reaction formonitrile or hydrocyanic acid.

Heated with free access of air, or in contact with metallic oxides, the KCy is further converted into potassium cyanate, KOCy.

REACTIONS IN SOLUTION.

A solution of potassium ferrocyanide may be used.

The alkaline ferrocyanides are readily soluble in water, the alkaline earthy ferrocyanides are difficultly soluble; those of iron and most other metals are insoluble in water, and many of them also insoluble in acids. They are decomposed on boiling with potassium hydrate with formation of a solution of potassium ferrocyanide, and an insoluble metallic hydrate. Some ferrocyanides are remarkable for characteristic colours, notably so those of iron and copper; others are white, *e.g.*, those of the alkaline earthy metals, of Zn, Pb, Ag, Hg; greenish-white, *e.g.*, Ni_2FeCy_6, Co_2FeCy_6; reddish-white, *e.g.*, Mn_2FeCy_6. Potassium ferrocyanide is employed, on this account, as a useful reagent in the qualitative examination of metals, and is especially useful in the detection of iron and copper.

$AgNO_3$ produces a white precipitate of silver ferrocyanide, Ag_4FeCy_6, insoluble in dilute nitric acid and ammonium hydrate, soluble in potassium cyanide.

$CuSO_4$, added in excess, gives, with a solution of K_4FeCy_6, a red chocolate-coloured precipitate of cupric ferrocyanide, Cu_2FeCy_6, whilst an insufficient amount of the cupric salt gives a brown precipitate of dipotassium cupric ferrocyanide, $K_2CuFeCy_6$.

√ $FeSO_4$ gives a light blue precipitate of potassium ferrous ferrocyanide, $K_2FeFeCy_6$, thus:

$$K_4FeCy_6 + FeSO_4 = K_2FeFeCy_6 + K_2SO_4,$$

which is slowly oxidised by exposure to the air, or rapidly, by oxidising agents, such as nitric acid, or chlorine water, to dark-blue Prussian blue.

Potassium ferrocyanide is, in fact, readily converted into potassium ferricyanide $K_6Fe_2Cy_{12}$ (analogous to the conversion of ferrous salts into ferric salts), by various oxidising agents, such as chlorine, nitric acid, potassium chlorate and hydrochloric acid, &c.

√ Fe_2Cl_6 gives an intensely blue precipitate of $Fe_4(FeCy_6)_3$, called Prussian blue, thus:

$$3K_4FeCy_6 + 2Fe_2Cl_6 = Fe_4(FeCy_6)_3 + 12KCl,$$

which constitutes at once a most characteristic and delicate reaction for ferric salts and for ferrocyanogen (as well as for cyanogen, as has been already shown). This precipitate is insoluble in dilute mineral acids, but dissolves in oxalic acid to a blue liquid (blue ink), and in ammonium tartrate to a violet liquid also used as an ink. It is decomposed by caustic alkalies, as well as by calcium, and even more readily and completely by magnesium carbonate (magnesite). On

boiling with mercuric oxide, Prussian blue is entirely decomposed into $HgCy_2$ and ferrous and ferric oxides, thus:

$$Fe_4(FeCy_6)_3 + 9HgO = 9HgCy_2 + 3FeO + 2Fe_2O_3.$$

By adding an insufficient amount of Fe_2Cl_6 to a solution of K_4FeCy_6, a blue precipitate is likewise obtained, which is, however, soluble in water, and is therefore called soluble Prussian blue (used for inks). It is generally thought to be composed of Prussian blue combined with potassium ferrocyanide.

Concentrated sulphuric acid (about 10 parts by weight) decomposes potassium ferrocyanide (1 part by weight of the dry salt), with evolution of carbonic oxide (method for preparing carbonic oxide); the nitrogen of the cyanogen, being converted into ammonia, is retained as ammonium sulphate, thus:

$$K_4FeCy_6 + 6H_2SO_4 + 6OH_2 = 6CO + 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4.$$

All cyanides, except those of silver, are decomposed in the same way.

When concentrated hydrochloric acid is added to an alkaline ferrocyanide, hydroferrocyanic acid separates from a cold solution as a white crystalline powder, which turns blue. If ether be added to the solution of potassium ferrocyanide, previous to the addition of the acid, it is obtained quite colourless. It is still better when gaseous HCl is passed into the ferrocyanide solution to which the ether has been added.

HYDROFERRICYANIC ACID, H_6FeCy_{12} *or* H_3FeCy_6.—Potassium ferricyanide is derived from K_4FeCy_6 by a process of oxidation, as, for instance, by passing chlorine into an aqueous solution of it, till a solution of ferric chloride no longer produces a blue precipitate, but imparts merely a brown coloration to the liquid. The change is expressed by the equation:

$$2K_4FeCy_6 + Cl_2 = K_6Fe_2Cy_{12} + 2KCl.$$

It is effected by the abstraction of two atoms of potassium from two molecules of K_4FeCy_6. Two atoms of cyanogen are transferred to two molecules of $FeCy_2$, whereby the ferrous cyanide is converted into ferric cyanide.

It is also called red prussiate of potash, on account of its colour.

Reducing agents convert it into potassium ferrocyanide, especially in alkaline solutions.

The following are instances of indirect oxidation effected by potassium ferricyanide:

SH_2 converts the ferri- into ferro-cyanide, with separation of sulphur.
KI „ „ „ with precipitation of iodine.

Cr_2O_3, or its salts, in the presence of KHO, is converted into					CrO_3.
PbO	"	"	"	"	PbO_2.
MnO	"	"	"	"	MnO_2.
SnO	"	"	"	"	SnO_2.
$H_2C_2O_4$	"	"	"	"	CO_2 and OH_2.
KCy	"	"	"	"	$KOCy$.
P_2O_3	"	"	"	"	P_2O_5.
SO_2	"	"	"	"	SO_3.

NH_3 gives with $K_6Fe_2Cy_{12}$ potassium and ammonium ferrocyanides with evolution of nitrogen, thus:

$$6K_6Fe_2Cy_{12} + 16NH_3 = 9K_4FeCy_6 + 3NH_4FeCy_6 + N_4.$$

Many organic substances, *e.g.*, sugar, dextrine, starch, alcohol, and even paper, *are oxidised, in the presence of an alkali*, to CO_2 and OH_2. Indigo is bleached. Phosphorus, sulphur, and iodine are converted by the action of $K_6Fe_2Cy_{12}$, in the presence of alkalies, into H_3PO_4, H_2SO_4, HIO_3.

Analogous to potassium ferrocyanide, the ferricyanide forms double ferricyanides, by the partial or entire replacement of the six atoms of the positive element, potassium, by different metals. The following are some of the more important metallic ferricyanides:

$K_6Fe_2Cy_{12}$	$Ba_2K_2Fe_2Cy_1 + 3OH_2$.
$Na_6Fe_2Cy_{12} + OH$	$Fe_3Fe_2Cy_{12}$ (Turnbull's blue).
$Ca_3Fe_2Cy_{12} + 6OH_2$.	

DRY REACTIONS.

Potassium ferricyanide is decomposed upon ignition, yielding cyanogen and nitrogen, and leaving a residue, consisting of potassium cyanide, potassium ferricyanide, Prussian blue, paracyanogen, carbon and iron.

REACTIONS IN SOLUTION.

A solution of potassium ferricyanide may be used.

The alkaline ferricyanides are readily soluble in water. The others are mostly insoluble.

$AgNO_3$ produces an orange-coloured precipitate of silver ferricyanide, $Ag_6Fe_2Cy_{12}$, insoluble in dilute nitric acid, but readily soluble in ammonium hydrate and potassium cyanide.

$FeSO_4$ gives a blue precipitate (Turnbull's blue) of $Fe_3Fe_2Cy_{12}$, ferrous ferricyanide, which is decomposed by potassium hydrate into potassium ferrocyanide and ferroso-ferric hydrate:

$$Fe_3Fe_2Cy_{12} + 8KHO = 2K_4FeCy_6 + Fe_3O_4,4OH_2.$$

Fe_2Cl_6 produces no precipitate, but gives a brownish coloration. The deportment of potassium ferro- and ferri-cyanide with iron salts distinguishes between ferrous and ferric salts.

HYDROCOBALTICYANIC ACID, $H_6Co_2Cy_{12}$.—Solutions of cobaltous salts are precipitated by KCy. The precipitate consists of flesh-coloured or cinnamon-brown cobaltous cyanide, $CoCy_2$. Excess of potassium cyanide rapidly dissolves the precipitate, forming a readily decomposable double cyanide $Co(Cy)_2(KCN)_4$, which on boiling in the presence of HCy, is converted into a difficultly decomposable double cyanide, analogous to potassium ferricyanide, with evolution of hydrogen, thus:

$$2Co(CN)_2 + 8KCN + 2H_2O = K_6Co_2(CN)_{12} + 2KHO + H_2.$$

This double cyanide is of interest, as its production affords one means of separating cobalt from nickel, both qualitatively and quantitatively.

The free acid can be obtained from copper cobalti-cyanide by the action of SH_2. It is soluble in water and alcohol, and is not decomposed by boiling with water or even fuming nitric acid, and dissolves zinc with evolution of hydrogen.

CYANIC ACID, or *Carbimide*, HCNO.—*Obtained in the form of potassium cyanate by the oxidation of* KCy. This salt is very stable when heated by itself, but deliquesces in the air, and is broken up by water into an acid carbonate and ammonia, thus:

$$KOCy + 2OH_2 = HKCO_3 + NH_3.$$

Potassium cyanate is invariably found in commercial potassium cyanide.

Potassium cyanate can be obtained by the oxidation of potassium ferro-cyanide in several ways. A simple method is to melt eight parts of dry $K_4Fe(CN)_6$ with three of K_2CO_3, and when the mass is just melted stir in gradually fifteen parts red lead. The mass is kept in fusion and stirred, so that the reduced lead may sink, and the melted KCNO then poured on a plate or tile.

REACTIONS IN SOLUTION.

The cyanates of the alkalies, alkaline earths, and a few metallic oxides are soluble in water, but decompose rapidly with evolution of ammonia. The silver, lead, mercurous, and cupric cyanates are insoluble in water.

Ammonium cyanate, NH_4CNO, undergoes a molecular change into urea $CO{NH_2 \atop NH_2}$ by simply warming its solution.

$AgNO_3$ produces with potassium cyanate a white precipitate of silver cyanate, AgOCy, soluble in ammonium hydrate, and in dilute nitric acid; AgCy is insoluble in nitric acid.

Moderately concentrated sulphuric or hydrochloric acid decomposes KOCy, with liberation of HOCy, which affects the eyes most painfully, and is recognised by its pungent odour, resembling that of strong acetic acid; a portion of the liberated acid, is, however,

decomposed at once by water into CO_2, and an ammonium salt, thus:

$$2KOCy + 2H_2SO_4 + 2OH_2 = 2CO_2 + K_2SO_4 + (NH_4)_2SO_4.$$

and it is by testing for ammonia in the residue from the reaction that the presence of HCyO can be shown under certain conditions. Part of the acid polymerises into cyanuric acid.

A number of cyanates of heavy metals decompose on heating into CO_2 and cyanimide salts, *e.g.*,

$$Ca(CNO)_2 = CaCN_2 + CO_2.$$

SULPHOCYANIC ACID, HSCy, is obtained in combination with potassium by heating KCy with sulphur or a metallic sulphide. Hence the usefulness of potassium cyanide for reducing metallic sulphides in blowpipe reactions. It also combines with sulphur when in solution.

Allyl sulphocyanate is present in mustard seed; the urine of a good many animals contains small but constant amounts of SCN compounds.

CS_2 heated with alcoholic NH_3 solution

$$CS_2 + 4NH_3 = CNSNH_4 + (NH_4)_2S.$$

Owing to this method of formation it is found in the ammonia water from the *coal-gas manufacture.*

Sodium Amide, $NaNH_2$, is produced by the action of sodium on ammonia gas. This when acted on by CS_2 gives:

$$NaNH_2 + CS_2 = NH_2CSNaS,$$

which breaks up into CNSNa and H_2S.

The free acid can be obtained in solution by decomposing $Hg(SCN)_2$ with SH_2. It is a colourless liquid which rapidly decomposes, sometimes explosively. A solution in water also decomposes rapidly unless very dilute. The dilute acid produces a red mark on paper which disappears on warming or after some time.

Warmed with dilute H_2SO_4, a sulphocyanate gives off COS, carbon oxysulphide, and an ammonia salt remains dissolved. Organic acids, as acetic, give an amide, or nitrile, and COS.

$$KSCN + 2CH_3CO_2H = KO_2CCH_3 + COS + \underset{\text{Acetamide}}{CH_3CONH_2}.$$

which again may give

$$\underset{\text{Acetonitrile}}{CH_3CN} + H_2O.$$

Chlorine produces from water solutions of sulphocyanates a bright yellow precipitate of $(SCN)_x$ pseudo sulphocyanogen. AgCl is converted completely into AgSCN on contact with a soluble sulphocyanate, and is consequently the best precipitant for SCNH, and is used for quantitative, volumetric, purposes.

DRY REACTIONS.

KCyS can be fused out of contact with the air, without undergoing decomposition. It turns first brown, then green, and lastly indigo-blue, but becomes again colourless on cooling. In contact with the air, KCyS is converted into cyanate and sulphate, with disengagement of SO_2. The sulphocyanates of the heavy metals are decomposed upon ignition, CS_2 being given off at first and on raising the temperature a mixture of nitrogen and cyanogen is evolved, whilst a metallic sulphide is left :

$$4Cu_2S_2Cy_2 = N_2 + 3C_2N_2 + 2CS_2 + 4CuS.*$$

Ammonium sulphocyanate gives some very complex resolution-products on heating in closed vessels.

REACTIONS IN SOLUTION.

A solution of ammonium sulphocyanate, NH_4SCN, is used.

$AgNO_3$ produces a white curdy precipitate of silver sulphocyanate, AgCyS, insoluble in water and in dilute acids; it is soluble in ammonium hydrate, from which it crystallises out on evaporation. If the ammonium hydrate is considerably diluted, the SCyAg will not appreciably dissolve, and AgCl and AgCy may be identified in the presence of SCyAg by this means. It is also soluble in AmSCy or KSCy, forming a double sulphocyanate, SCyAg,SCyK, from which water or hydrochloric acid precipitates granular, ammonium hydrate, crystalline, SAgCy.

$CuSO_4$ gives a black crystalline precipitate of cupric sulphocyanate, CuS_2Cy_2, which is converted into white cuprous sulphocyanate, $Cu_2S_2Cy_2$, by the action of sulphurous acid.

Fe_2Cl_6 produces an intensely red solution, owing to the formation of a soluble ferric sulphocyanate, $Fe_2(SCN)_6$. Alkaline sulphocyanates are most delicate reagents for ferric salts. This reaction serves also for the detection of sulphocyanogen and hydrocyanic acid. The blood-red colour is destroyed by $HgCl_2$. On introducing some metallic zinc into the blood-red solution, SH_2 is evolved.

All organic acids other than the hydrocyanic acids contain at least one negative group, containing a replaceable hydrogen atom, of the form —CO.OH (carboxyl), the molecule of which $\begin{array}{c}\mathrm{OC.OH}\\ | \\ \mathrm{OC.OH}\end{array}$, constitutes oxalic acid, a body resulting from the oxidation of a large number of organic bodies, *e.g.*, sugar, woody fibre, &c., by the action of powerful oxidising agents such as concentrated nitric acid, and is, on further oxidation, itself resolved into the products of the final

* This copper salt is also very slightly soluble and is employed as a means of quantitative separation of copper from several other metals.

oxidation of everything organic, viz., carbonic anhydride and water. This group – COOH is characteristic of organic acids.

Heats breaks up nearly all salts of organic acids. Those of alkaline and alkaline earthy bases leave upon gentle ignition carbonates, with separation of carbon, and consequent blackening, oxalates excepted. The residue, with the exception of the carbon, being soluble in water, indicates that the organic acid was combined with alkali metals, and if insoluble, with alkaline earthy bases. The decomposition is, moreover, accompanied in most instances by the evolution of volatile matter, of carbonic oxide, hydrocarbons, acetone, and other products. Some metallic salts leave metal or oxide.

In the free state organic acids are either volatile, and can be *distilled or sublimed, generally without undergoing decomposition* and without leaving any carbonaceous residue, as for instance, formic, acetic, benzoic, and many others. Most of these acids can be displaced by mineral acids as sulphuric. Some organic acids are non volatile, and are decomposed on heating alone, leaving generally a residue of carbon. Many of these acids will, however, distil in a current of steam without decomposition. Some are also more soluble in liquids, as ether, chloroform, petroleum, than in water, and may be by these means separated.

FORMIC ACID, $\left.\begin{matrix} H \\ O:C.OH \end{matrix}\right\}$ exists in many plants, and can be exuded under certain conditions by some animals, for instance ants. It can be obtained by the oxidation of methyl alcohol, $CH_3.OH$, by platinum black.* The action of glycerine on oxalic acid gives one of the easiest methods of obtaining formic acid in quantity. The reaction takes place in several stages, glycerol monoformin being one. Equal weights of the two substances are heated together in a retort to 100° C., when the formic acid distils over with the water. Dry formic acid is a liquid above 8·5° C.; it boils at 99° C., and has a specific gravity = 1·22. It is monobasic. Oxidising agents convert it into CO_2 and OH_2. *Its salts give the same reactions.*

DRY REACTIONS.

Formates of the fixed alkalies and alkaline earthy bases, when heated out of contact with air, are decomposed into carbonates, and a little carbon, with disengagement of combustible gases—mainly carbonic oxide and hydrogen. Formates of the heavy metals give off CO_2, CO, and OH_2, leaving the metal (generally mixed with a little carbon).

* This method is of interest as showing its constitution and its relation to the alcohols and carbinols, of which CH_3OH is the simplest, as is formic the simplest organic or carboxylic acid.

This experiment may be performed in a flask with wide neck. A few cc.'s of methyl alcohol are introduced, and then a red hot platinum wire spiral lowered into the flask, not touching the alcohol; the wire continues to glow and some formic aldehyde, HCOH, is first produced. Some of this oxidises further, producing HCOOH. The residue in the flask will be found to be acid to litmus.

REACTIONS IN SOLUTION.

A solution of sodium formate, $\begin{matrix}H\\OCONa\end{matrix}$, gives the reactions.

All formates are soluble in water, lead formate least so; some also in alcohol.

Formic acid and formates are readily recognised by their property of reducing salts of the noble metals, *e.g.*, $AuCl_3$, $AgNO_3$, $Hg_2(NO_3)_2$, or $HgCl_2$, to the metallic state, with evolution of carbonic anhydride.

Mercuric chloride solution warmed with a little formic acid or formate and HCl gives a white precipitate of Hg_2Cl_2—

$$2HgCl_2 + HCOOH = Hg_2Cl_2 + CO_2 + 2HCl.$$

On boiling, the reaction goes further, and Hg is formed.

This reducing action distinguishes formic acid from acetic acid and some of its homologues.

Potassium permanganate is rapidly deoxidised by formic acid.

Formic acid or a formate, when heated with a solution of potassium dichromate and sulphuric acid, is broken up, with evolution of CO_2.

When heated with concentrated sulphuric acid, formic acid and formates are broken up into water and carbonic oxide, which latter burns with a blue flame. (Method of preparing carbonic oxide gas (see *ante*). The mixture does not blacken.

$$HCOOH - H_2O = CO.$$

Formic acid may be synthetised by heating carbon monoxide and potassium hydrate to about 100° C.

$$KHO + CO = KOOCH;$$

or soda lime, moist, to 190°–200°; also from HCN by the action of KHO, thus:

$$HCN + \begin{Bmatrix}H_2O\\KOH\end{Bmatrix} = H.C\begin{matrix}O\\OK\end{matrix} + NH_3.$$

(See Cyanogen.)

Formic acid heated with zinc gives CO and H.

ACETIC ACID, $\begin{matrix}CH_3\\OC.OH\end{matrix}$.—Is obtained either by the oxidation of alcohol, thus:

$$\begin{Bmatrix}CH_3\\CH_2OH\end{Bmatrix} + O_2 = \begin{matrix}CH_3\\OC.OH\end{matrix} + OH_2,$$

or by the destructive distillation of vegetable substances, especially of wood and organic acids containing much oxygen. The acid can be

synthetised in several ways, from methylcyanide with KHO; from sodium methyl, CH_3ONa and CO at 160° = $NaOOCCH_3$, &c. Chromic acid, or permanganate, will oxidise alcohol to acetic acid, but in almost every case of oxidation some aldehyde is first formed.

In the ordinary method of preparation the oxidation of the alcohol is carried on by the agency of a bacterium, which can function in very dilute alcohol solution. It practically conveys atmospheric oxygen to the alcohol.

The main source of commercial acetic acid is the liquid distillate obtained during wood charcoal making, the woody matters being charred in iron vessels and the volatile matters carefully condensed. (For details, see "Practical Organic Chemistry.")

Pure anhydrous acetic acid boils at 118° C. This is termed glacial acetic acid, and is prepared by decomposing dry sodium acetate (5 parts by weight) with concentrated sulphuric acid (6 parts by weight) and distilling. The crude acid is placed over MnO_2, in order to remove any SO_2, and rectified by distillation over a little dry sodium acetate. It crystallises when nearly pure.

DRY REACTIONS OF ACETATES.

Acetates are decomposed when distilled in a retort or similar partially closed vessel, yielding an inflammable volatile liquid—acetone.

$$\begin{array}{c} CH_3 \\ OCO \\ OCO \\ CH_3 \end{array}\!\!>Ca = CaCO_3 + \begin{array}{c} CH_3. \\ CO\ . \\ CH_3. \end{array}$$

Calcium acetate — Acetone.

The acetates of the alkalies and alkaline earthy bases, when strongly heated in the air, leave a carbonate; those of the heavy metals leave either a metallic oxide, or the metal itself, mixed with carbon,

$$2(AgO_2CCH_3) = 2Ag + \underset{\text{Acetic anhydride}}{(CH_3CO_2)_2O} + O;$$

this should be the action with silver acetate. Some acetic anhydride is produced and the oxygen instead of coming off as such oxidises some of the acetic molecule to CO_2 and H_2O.

Heated with alkaline hydrates, dry sodium acetate gives off marsh-gas, or methane, CH_4, thus:

$$\begin{array}{l} CH_3 \\ OCONa \end{array} + NaHO = Na_2CO_3 + CH_4.$$

The gas can be collected in the usual manner over water, and on applying a light it burns quietly with an almost non-luminous flame to water and carbonic anhydride. It generally contains a few per cents. of hydrogen.

REACTIONS IN SOLUTION.

A solution of sodium acetate may be employed.

All acetates are soluble in water. Silver and mercurous acetates are the least soluble.

On heating a solid acetate (or a concentrated aqueous solution of one) with alcohol and concentrated sulphuric acid, acetic ether (ethylic acetate), $CH_3C.O.OC_2H_5$, is formed, which possesses a fragrant odour. The change is expressed thus:

$$CH_3COONa + C_2H_5OH + H_2SO_4 = \begin{cases} CH_3 \\ C.O.OC_2H_5 \end{cases} + HNaSO_4 + OH_2.$$

Too much alcohol should be avoided lest common ether, $O(C_2H_5)_2$, be formed, the odour of which would mask that of the acetic ether. Acetates of a dibasic metal like Ca or Ba when heated alone in a retort or similar closed vessel, yield more acetone than an alkaline acetate, where much CH_4 accompanies the acetone.

By distilling an acetate with moderately dilute sulphuric acid in a retort, free acetic acid is obtained, which is recognised by its characteristic pungent odour. Acetic acid is not easily oxidised by chromic acid when very pure or glacial, more easily when dilute, but still not rapidly.

Fe_2Cl_6 added to a solution of an acetate, produces a deep red coloured solution, owing to the formation of ferric acetate. On boiling, the whole of the iron is precipitated as basic ferric acetate, in the form of brownish-yellow flakes. NH_4OH precipitates the iron from a solution of ferric acetate as ferric hydrate.

Ammonium acetate, especially in the presence of ammonia, dissolves several insoluble sulphates, *e.g.*, $PbSO_4$, $CaSO_4$.

Ammonium acetate on being heated in a retort decomposes, giving off water and leaving acetamide, a body of most characteristic odour, something like mice, or mice excrement, which contains it.

$$CH_3COONH_4 = H_2O + CH_3.CO.NH_2.$$

Dry acetates heated with arsenious acid, As_2O_3, give cacodyl, CH_3AsCH_3, readily distinguished by its onion-like odour. It is highly poisonous. This reaction, if performed at all, should only be done on the smallest scale.

*Approximate Separation of Acetic Acid from its next higher Homologues.**—Add enough potassium or sodium hydrate to convert the acetic acid into acetate and distil. The acid containing the least number of carbon atoms, being the stronger, is first neutralised, and if sufficient potash has been added, the distillate is obtained free from acetic acid. One or two repetitions of this treatment will give a salt containing only traces of the homologues of acetic acid.

* Homologues of acetic acid are propionic, CH_3CH_2COOH, butyric, $CH_3CH_2CH_2COOH$, and so on. They differ from acetic by containing a CH_2 more in the molecule. Otherwise their basicity and general properties are very much the same. (See Organic.)

BENZENE,* C_6H_6. Specific gravity 0·85 at 15·5°. Boiling point 80·4° at 760 mm.—Is a liquid which, when cooled below 0° C., solidifies into fern-like tufts, melting again at 5·5° C. It is a non-conductor of electricity. At the ordinary temperature it is a limpid, colourless, strongly refracting liquid, having a pleasant odour; slightly soluble in water, imparting a strong odour to it, readily soluble in ether, wood spirit, and acetone. It dissolves sulphur, phosphorus, and iodine, especially on heating, fixed and volatile oils, camphor, wax, caoutchouc, &c.

Benzene is very inflammable, and burns with a bright smoky flame. When its vapour is passed through a red-hot tube, carbon is separated, and gaseous and solid hydrocarbons (diphenyl principally) are formed. Chlorine and bromine act upon it in sunshine, forming both addition and substitution products. It is not acted upon by alkalies, but potassium acts upon it forming a blue-coloured compound which is explosive, or explodes on contact with water. Strong nitric acid converts its into nitrobenzene.

$$C_6H_6 + HNO_3 = C_6H_5NO_2 + H_2O.$$

Sulphuric anhydride or fuming sulphuric acid converts it into sulphobenzide $(C_6H_5)_2SO_2$, ordinary sulphuric acid into $C_6H_5HSO_3$.

Detection.—The liquid to be tested is warmed in a test-tube with strong nitric acid; diluted with water, and shaken up with ether, which dissolves the nitrobenzene.

The ethereal solution is mixed with a little alcohol and strong HCl, and a few pieces of zinc added. After about five minutes rapid evolution of hydrogen from the zinc the solution is poured off, excess of KHO added, and then if the aniline formed be in too small quantity to separate, ether is added, and the ethereal solution separated and evaporated on a watch-glass. On adding a few drops of chloride of lime solution to the oily residue on the watch-glass, a purple colour is formed if aniline and therefore benzene be present.

Nitrobenzene is reduced by nascent hydrogen to aniline, thus:

$$C_6H_5NO_2 + 3H_2 = 2H_2O + C_6H_5NH_2.$$

PHENOL, $C_6H_5.OH$ (carbolic acid), is the hydrate of benzene; it occurs in heavy coal-tar oil, in castor-oil, and in the urine of some herbivorous animals.

When pure, phenol consists of large colourless prisms of a peculiar odour, and giving a burning taste. It melts at 42°, and boils without decomposition at 181·5°. When not quite pure it is slightly coloured red or brown. Phenol is soluble in 15 parts of cold water, but much more readily in alcohol. Its solution is a powerful antiseptic and caustic, and it is also highly poisonous.

Bromine water added to a phenol solution forms tribromophenol,

* Benzene is not an acid, and is only introduced here because it is the groundwork or parent substance of a number of real organic acids and some bodies which act something like acids.

a yellow solid, which is somewhat insoluble, 1 part in 60,000 of water, and therefore precipitates. Concentrated nitric acid converts it into trinitrophenol or picric acid, which unites with alkalies, and is soluble in alcohol; this solution dyes silk or wool yellow. On adding ammonia to a phenol solution, and then a hypochlorite or hypobromite, a fine blue colour is produced.

Ferric chloride, added to a solution of phenol in water, produces a fine purple colour (1 part in 3000 water). Albumen solution is coagulated on addition of phenol. Phenol boiled with Millon's reagent (mercuric nitrate with excess of nitric acid), produces a fine red colour, permanent for some time.

SALICYLIC ACID, $C_6H_4{}^{.OH}_{.OCOH}$, exists in Nature in combination with methyl alcohol in oil of winter green (*Gaultheria procumbens*), and in saligenin, contained in willow bark, &c. It may also be formed by heating the ortho-haloid benzoic acids with potash,

$$C_6H_4.Br.COOH + KHO = C_6H_4(OH)COOK + KBr + H_2O.$$

It is made on a large scale by Kolbe's reaction, heating sodium phenol in CO_2 to 190° C. Phenol distils, and sodium salicylate remains in the retort.

$$2(C_6H_5.ONa) + CO_2 = C_6H_4ONaCOONa + C_6H_5OH.$$

Salicylic acid is monobasic; it dissolves slightly in cold water, more easily in hot, in alcohol and ether. It melts at 156° C., and distils in steam. Its aqueous solution gives a fine violet solution with Fe_2Cl_6. This colour is destroyed by mineral acids and by alkalies. 1 part in 100,000 OH_2 is indicated by this test. It is a powerful antiseptic.

On distilling salicylic acid with excess of lime, phenol is produced.

$$C_6H_4{}^{OH}_{COOH} + CaO = CaCO_3 + C_6H_5OH.$$

Salicylic acid	Lime	Calcium carbonate	Phenol

$AgNO_3$ gives a white precipitate with salicylates
Lead acetate gives a white precipitate with salicylates } but *not* with the free acid.

Bromine water added to solutions of salicylic acid gives a white crystalline precipitate of tribromsalicylic acid, similar to phenol.

With Millon's reagent a similar red colour is produced to that with phenol.

BENZOIC ACID, $C_6H_5.CO.OH$.—Is found in many gums and balsams, from which it is obtained by sublimation. Heated in a tube open at both ends, the acid sublimes in long needles, giving off a pleasant smelling but irritating vapour. Heated on platinum foil, benzoic acid burns with a luminous smoky flame.

The acid is very slightly soluble in cold water, 200 parts cold, 12 parts boiling. It is readily soluble in alcohol, ether, &c. Benzoates of tetrad metals are mostly insoluble in water, all others are soluble.

Fe_2Cl_6 gives a pale yellow precipitate of basic ferric benzoate, $(C_6H_5CO_2)_6Fe_2.Fe_2O_3 + 15OH_2$; and ammonium benzoate is employed sometimes for the separation of Fe^{iv} from Mn''.

On distilling benzoic acid or benzoates, with lime or baryta, benzene, C_6H_6, is obtained—

$$\begin{cases} C_6H_5 \\ CO.OH \end{cases} + CaO = C_6H_6 + CaCO_3,$$

which may be made into nitrobenzene by HNO_3, and this into aniline. (See Benzene.)

Dilute acids precipitate benzoic acid from aqueous solutions of benzoates; dilute nitric acid is without action upon the acid itself.

Heated with concentrated sulphuric acid, benzoic acid does not blacken, neither does it evolve SO_2.

Vapour of benzoic acid passed over heated zinc dust in a tube gives odour of bitter almonds, benzoic aldehyde, $C_6H_5.COH$. Also when a solution of a benzoate is acidified with H_2SO_4 and a piece of Mg immersed therein the same odour is produced.

Benzoic acid is "phenyl" formic acid. C_6H_5 functions in the place of H in formic acid. $C_6H_5.COOH$.

SUCCINIC ACID, $\begin{cases} COOH \\ C_2H_4 \\ COOH \end{cases}$—This acid is dibasic. It is obtained by the distillation of amber, of fossil resin, and also by the long-continued action of nitric acid upon butyric, stearic, or margaric acids, by fermentation of sugar, malic acid, glycerine, &c. The acid crystallises in white plates, is readily soluble in water, alcohol, and ether, and is not acted upon by boiling nitric acid. Heated in a tube open at both ends, it sublimes in silky needles. Heated upon platinum foil, it burns with a blue flame and without smoke. It melts at 180° C., but gives off fumes at 130° C. At 235° C. it boils and forms the anhydride.

Succinates are decomposed upon ignition; the alkaline and alkaline earthy succinates leave a carbonate mixed with carbon.

Most succinates are soluble in water.

Lead acetate gives a white precipitate of neutral lead succinate, $\begin{cases} CO—O \\ C_2H_4Pb \\ CO—O \end{cases}$ which is rendered basic by treatment with ammonium hydrate.

Fe_2Cl_6 produces from a solution of neutral ammonim succinate a brownish-red, voluminous precipitate of basic ferric succinate, $(C_4H_4O_4)_3Fe_2Fe_2O_3$, readily soluble in mineral acids. NH_4OH renders the precipitate darker by withdrawing a quantity of succinic acid as ammonium succinate, leaving a more basic succinate. (This reaction serves for the separation of Mn'' from Fe^{iv}.)

On boiling the precipitate produced by ferric chloride from a solution of a succinate or benzoate, with ammonium hydrate, soluble ammonium salts of these acids are obtained which can be separated by filtration from the insoluble residue. On the addition of alcohol and $BaCl_2$ to the ammoniacal solution, a white precipitate of barium succinate is obtained, whilst benzoic acid gives no precipitate (distinction between benzoic and succinic acids).

Succinic acid is insoluble in chloroform. Benzoic is soluble. Magnesium benzoate is also soluble in alcohol, but the corresponding succinate is not.

Succinic acid is ethylene dicarboxylic acid.

OXALIC ACID, $\begin{cases} COOH \\ COOH \end{cases}$.—"Dicarboxyl."—Exists in rhubarb, sorrel, and other plants in the form of acid salts, and may be obtained by the oxidation of a large number of organic bodies, *e.g.*, sugar by nitric acid; or woody fibre, by the action of caustic alkalies. The free acid is a violent poison. It crystallises in rhombic prisms with two molecules of water of crystallisation, which it loses when exposed to dry air, *i.e.*, it effloresces and crumbles to a powder. With bases it forms an important series of salts, called oxalates. The acid being dibasic, two series of salts, neutral and acid, $\begin{matrix} OCOK \\ OCOK \end{matrix}$ and $\begin{matrix} OCOK \\ OCOH \end{matrix}$, exist besides some super acid oxalates.

Oxalic acid may be looked upon as the hydrate of the unknown oxide of carbon, C_2O_3.

DRY REACTIONS.

Oxalic acid when heated by itself, loses its crystal water, and then sublimes for the most part unchanged; a portion of it breaks up into CO, CO_2 and some formic acid. Oxalates yield, upon ignition, different products of decomposition, according to the nature of the base contained therein.

Alkaline oxalates leave a carbonate, with slight blackening, and give off carbonic oxide.

Alkaline earthy oxalates leave a carbonate, together with some caustic base, if a strong heat be applied, and give off CO and CO_2.

Oxalates containing metallic bases which do not form carbonates, or the carbonates of which are decomposed by heat, break up into metallic oxides, and give off equal volumes of CO and CO_2, or into metal, as for instance silver oxalate, which gives off CO_2.

Heated with strong H_2SO_4 oxalates and the acid decompose into CO_2 and CO, which escape together.

REACTIONS IN SOLUTION.

Use a solution of ammonium oxalate.

Beside the alkaline normal oxalates very few are soluble in water. Mineral acids dissolve the insoluble oxalates by forming perhaps acid oxalates.

Any soluble calcium salt precipitates even from very dilute solutions white pulverulent calcium oxalate, readily soluble in hydrochloric or nitric acid; almost insoluble in oxalic or acetic acid, and in potassium or ammonium hydrate. Heat promotes the precipitation from very dilute solutions. This constitutes one of the most delicate *reactions for oxalic acid.*

$BaCl_2$ gives from solutions of neutral oxalates a white precipitate of barium oxalate, soluble in oxalic acid, readily soluble in hydrochloric or nitric acid.

$AgNO_3$ produces a white precipitate of silver oxalate, $\begin{matrix} COOAg \\ | \\ COOAg \end{matrix}$, soluble in dilute nitric acid, and in ammonium hydrate.

Concentrated sulphuric acid decomposes oxalic acid or oxalates, on warming only, into CO and CO_2, without blackening, by withdrawing from the molecule of oxatyl a molecule of OH_2. The gaseous mixture is passed through a wash-bottle containing caustic soda or lime-water, and the carbonic oxide gas is collected over water. (Usual method for preparing carbonic oxide.)

Oxalic acid or oxalates in the presence of free mineral acids, act as reducing agents.

Treat a little black oxide of manganese and oxalic acid, or an oxalate, with a few drops of concentrated sulphuric acid. Effervescence ensues. The gas which escapes is carbonic anhydride, resulting from this reaction:

$$MnO_2 + \begin{matrix} OCOK \\ OCOK \end{matrix} + 2H_2SO_4 = 2CO_2 + MnSO_4 + K_2SO_4 + 2OH_2.$$

A solution of gold is reduced to metallic gold, thus:

$$2AuCl_3 + 3\begin{matrix} OCOH \\ OCOH \end{matrix} = 6CO_2 + Au_2 + 6HCl.$$

Potassium permanganate is speedily reduced (decolorised). The free acid dissolves in alcohol, both hot and cold, but not in chloroform or benzene.

Some of the Cerite metals, as Cerium, Lanthanum, Didymium, give oxalates *insoluble* in moderately strong HCl.

TARTARIC ACID, $\begin{matrix} OC.OH \\ HCOH \\ HCOH \\ OCOH \end{matrix}$.—This acid is dibasic.—It is found in grapes, tamarinds, pine-apples, and several other fruits in the form of hydrogen potassium tartrate. The acid met with in commerce is prepared from the tartar or argol, an impure hydrogen potassium tartrate, deposited from the grape juice during fermentation. The acid forms colourless transparent crystals, very soluble in water, both hot and cold, and soluble also in alcohol. The aqueous

solution undergoes gradual decomposition. There are five modifications of tartaric acid due to structural differences in the molecule.

DRY REACTIONS.

Tartaric acid is decomposed by heat, giving off an odour resembling that of burnt sugar (caramel), and leaving a residue of carbon. Alkaline tartrates when heated in a test tube, are decomposed with evolution of inflammable gases, leaving a mixture of finely divided charcoal and carbonate (black-flux), from which the carbonate may be extracted by water. The carbonaceous residue left upon igniting alkaline earthy tartrates contains an insoluble carbonate, and effervesces when treated with dilute hydrochloric acid. Tartrates of the heavy metals also undergo decomposition, accompanied by the characteristic odour of burnt sugar, and leave much carbon mixed with metallic oxide or metal.

REACTIONS IN SOLUTION.

Use a solution of tartaric acid, and for some reactions a solution of a normal salt, as Rochelle salt, potassium sodium tartrate.

The alkaline tartrates are soluble in water, the acid salts less so than the neutral tartrates. The normal tartrates of the alkaline earthy bases, of the earths and heavy metals, are difficultly soluble in water, but dissolve readily in dilute tartaric acid. Alkalies fail to precipitate double tartrates containing an alkaline and metallic base. Hence the presence of tartaric acid serves to prevent the precipitation of Fe_2O_3, Cr_2O_3, ZnO, NiO, CoO, MnO, CuO, PbO, Bi_2O_3, PtO_2, or CdO, whilst some other substance, *e.g.*, phosphoric acid, if present, may be precipitated from an alkaline solution.

KCl (or other potassium salt, especially a very soluble one) produces in a solution of free tartaric acid a heavy white crystalline precipitate of hydrogen potassium tartrate, readily soluble in mineral acids and in alkalies and alkaline carbonates, insoluble in acetic acid. The precipitation is accelerated by agitation and by allowing to stand for some hours. Alkalies dissolve the precipitate, forming a normal tartrate, soluble in water, from which acetic acid reprecipitates the acid salt.

$Ca(HO)_2$ added in excess to free tartaric acid precipitates white calcium tartrate.

$CaCl_2$ (but not $CaSO_4$, except on long standing) precipitates from a solution of a normal tartrate, white calcium tartrate, soluble in acids, even tartaric acid, in ammonium salts, but not in ammonium hydrate. The precipitate, especially as long as it is amorphous, *i.e.*, recently precipitated, is soluble in cold potassium or sodium hydrate, when nearly free from carbonate, but is reprecipitated on boiling as a gelatinous mass which redissolves on cooling.

$AgNO_3$ produces from a solution of a normal tartrate (*e.g.*, Rochelle salt) in the cold a white curdy precipitate of silver tartrate. On filtering and dissolving some of the precipitate off the filter with a little dilute ammonium hydrate, and heating the solution in a clean

test-tube or flask during ten or twenty minutes, in water, heated to about 60° C., the glass becomes coated with a fine silver mirror.* (Characteristic reaction for tartaric acid.)

Lead acetate gives a white crystalline precipitate of lead tartrate, from solutions of tartaric acid, or its soluble salts. The precipitate is soluble in nitric acid and in ammonium hydrate; the latter giving rise to the formation of lead ammonium tartrate, which cannot be precipitated by ammonia.

Tartaric acid and ammonia dissolve lead sulphate.

Concentrated H_2SO_4 decomposes tartaric acid, or a tartrate, on heating, with evolution of SO_2, CO_2 and CO, and separation of carbon.

CITRIC ACID, $\begin{matrix} OH \\ HC.CO.OH \\ HC.CO.OH \\ H_2C.CO.OH \end{matrix}$. — Tribasic. — Obtained from orange or lemon juice. Found also in many other fruits. It forms colourless prismatic crystals, which possess a pure and agreeable acid taste. They dissolve in cold and hot water, and in alcohol. The aqueous solution undergoes decomposition after a time. The citrates are very numerous, the acid forming, like phosphoric acid, three classes of salts by the replacement of one, two, or three atoms of hydrogen by an equivalent amount of a metal. There are no absolutely insoluble citrates.

DRY REACTIONS.

On heating citric acid, it loses first its water of crystallisation, then fuses, and is decomposed with disengagement of pungent and irritating acid fumes into aconitic acid, and finally to citraconic anhydride, leaving a less abundant carbonaceous residue than tartaric acid. Alkaline and alkaline earthy citrates leave a carbonate upon ignition.

REACTIONS IN SOLUTION.

Use a solution of citric acid in water, or a solution of a normal alkaline citrate.

Potassium salts give no precipitate.

$Ca(HO)_2$ gives no precipitate in the cold from a solution of citric acid, or of a neutral citrate; but on heating, a white precipitate of calcium citrate is obtained. (Distinction between tartaric and citric acid.) When both citric and tartaric acid are present, the precipitate produced by $Ca(HO)_2$ or $CaCl_2$ in the cold is filtered off, and the clear filtrate boiled, when a further precipitate indicates citric acid.

$CaCl_2$ produces at first no precipitate in the cold from an aqueous solution of citric acid, or a soluble citrate; but on standing, precipitation takes place and is all but completed even in the cold, after 24 hours. On boiling, a white precipitate of calcium citrate is obtained

* The presence of a little free NaHO or KHO accelerates the formation of the silver mirror.

if the solution be neutral, or if it contain an excess of lime-water or ammonium hydrate. This precipitate is insoluble in sodium or potassium hydrate, but soluble both in ammonium salts and in acids.

Silver nitrate dissolved in ammonium hydrate does not form a mirror upon heating, but a black deposit takes place after boiling for some time. Citric acid, like tartaric acid, prevents the precipitation of certain oxides, especially of Al_2O_3, Fe_2O_3, of Groups II. and III. and some phosphates by caustic alkalies on account of the formation of soluble double citrates, containing an alkali base and a heavy metal.

Concentrated sulphuric acid decomposes citric acid or citrates slowly. On cautiously applying heat, CO and CO_2, escape, at first without any blackening of the liquid, but on boiling for some time SO_2 is evolved and carbon separates.

UREA, $CO{\begin{matrix}NH_2\\NH_2\end{matrix}}$.—Is the chief form in which the waste nitrogen of the body escapes in the urine. It was synthetised by Wöhler from ammonium cyanate, NH_4OCN, which undergoes a molecular change on the evaporation of its solution. It was previously made by J. Davy, but not fully recognised.

Urea forms colourless crystals, which deliquesce in moist air; they are easily soluble in water and alcohol, but scarcely in ether. It melts at 130° C., and it then begins to decompose into cyanuric acid and biuret.

Heat a little urea in a test-tube until ammonia is evolved, add warm water; biuret dissolves, and on adding a little $CuSO_4$ solution, and then excess of NaHO, a violet colour is produced. Oxalic acid, added to a solution of urea, gives a crystalline precipitate of the oxalate, rapidly from strong, after some time from dilute, solutions.

Nitric acid, quite free from lower oxides of N, forms urea nitrate, which is also crystalline and soluble in water; very slightly so in nitric acid.

Mercuric nitrate precipitates from urea solutions, when the latter is in excess, white $(CON_2H_4)_2(HgO)_3$.

This precipitate is sometimes employed in the estimation of urea quantitatively.

Urea heated with KHO gives NH_3, ammonium carbonate being first formed.

Nitrous acid, or an acid solution of a nitrite, decomposes urea, liberating N and CO_2.

$$CON_2H_4 + 2HNO_2 = 2N_2 + CO_2 + 3OH_2.$$

Alkaline hypobromite or hypochlorite causes immediate effervescence, all the nitrogen being liberated.

$$CON_2H_4 + 3NaOBr + 2NaHO = N_2 + 3NaBr + 3OH_2 + Na_2CO_3.$$

CELLULOSE $(C_6H_{10}O_5)_n$, occurs in an approximately pure state in cotton, flax, and wood-fibre generally. It occurs in most plant-tissues, and may be considered as the skeleton or basis of the vegetable kingdom. Manufactured cotton, linen, paper, &c., represent more or less impure conditions of this substance.

Although its chemical composition is very close or perhaps identical with that of the starches and some other carbohydrates, it is well distinguished by its insolubility in water and most other reagents. Its microscopic structure varies with the source, but its chemical character is quite definite. To isolate cellulose from almost any vegetable matters (cotton-wool, or filter paper), treat with cold bromine water for 15 minutes and then boil in dilute ammonia. Repeat this treatment until the material has become quite white and the ammonia ceases to dissolve anything more.

It is doubtful if there be any simple solvent for cellulose in the sense that water is for sugar.

Concentrated acids, as H_2SO_4, HNO_3, and acetic dissolve it slightly, under certain conditions of temperature, undoubtedly forming salts with it. Zinc chloride is one of such solvents.

With powerful bases as $Ba(HO)_2$ and KHO it seems to form salts, acting as the negative or acid radical towards the strong base.

Unlike starch cellulose is not turned blue by iodine, but any cellular tissue moistened with a solution made by dissolving equal weights of zinc chloride and potassium iodide in strong HCl (Schultz's reagent), and then washing the brown stain with water, becomes blue or purple.

Cupra-ammonia, $Cu{}^{NH_2}_{NH_2}$, made by dissolving copper oxide in strong ammonia solution, dissolves cellulose to a thick gummy solution. The fibres are observed first to swell considerably before dissolving.

This solution, when diluted very largely with water or an acid, deposits cellulose in a gelatinous form.*

STARCH $(C_6H_{10}O_5)$.†—May be considered as an isomeride of cellulose. It occurs in nearly all parts of plants. It is most abundant in the grain of cereals, and in tubers like potato. In all cases it exists in cells, which vary in size and shape, depending on the plant.

Starch is insoluble in cold water, and is separated from grain or potatoes by trituration and washing by a stream of water. The cells are carried away from the cellular tissue, &c., and fall as a white powder on allowing the water to stand for some time.

The grains or cells of starch from any one source are moderately regular in shape; those from cereals are smaller than from tubers.

* Jute, cork, the mass of which apples, turnips, &c., consist, are probably modifications from cellulose or compound or oxycelluloses. A good deal of work is still required at these bodies to settle their nature definitely.

† See Cross and Bevan (*Chem. Soc. Journ.*) and separate publications.

On heating in a closed tube starch decomposes in a similar manner to woody fibre, giving off water and combustible gases, and leaving charcoal.

Shake up some starch with cold-water in a test-tube; it does not dissolve and will settle to the bottom unchanged on standing. Add twice its volume of boiling water, and shake. The mass forms a semi-transparent jelly. On heating to boiling, or nearly so, apparently complete solution takes place. Add an alcoholic solution of iodine or a solution of iodine in potassium iodide to a starch emulsion, a fine blue colour—iodide of starch—is produced. The colour varies from purple to blue. It is destroyed on heating, but reappears on cooling. (See tests for Nitrites.)

A starch solution, when heated for some time with a little acid, HCl or H_2SO_4, or with partially germinated grain solution, undergoes several changes.

DEXTRINE.—Dilute a few cc. of a starch solution made as above, add a few drops of HCl or H_2SO_4, dilute, and heat to nearly boiling. Pour out a few drops from time to time into an iodine solution, until only a brown coloration is produced. At this point the starch has been converted into an isomeride termed dextrine, which may be precipitated in a flocculent state by adding alcohol to the acid solution.

GLUCOSE (Dextrose or Grape-sugar).—A dilute solution of starch when boiled with addition of a few drops of HCl or H_2SO_4, until no further reaction is given with iodine, becomes converted into glucose.

$$C_6H_{10}O_5 + H_2O = C_6H_{12}O_6.$$

Grape-sugar is formed in many plants or fruits; from grapes which contain about 14 per cent. to peaches with little more than 1, in honey along with lævulose, and in diabetic urine. Dextrose crystallises from water as $C_6H_{12}O_6.OH_2$. It dissolves in $1\frac{1}{5}$ its own weight of water.

All glucoses, when warmed with alkaline copper tartrate, cause a yellow or red precipitate of Cu_2O, cane-sugar, dextrine, gum arabic, glycerine, urea, and a number of organic acids do not reduce the copper solution, or only after long boiling.

$2C_6H_{12}O_6$ reduces 10CuO.
Glucose

$C_{12}H_{22}O_{11}$ reduces 7CuO.
Lactose

$C_{12}H_{22}O_{11}$ reduces 6CuO.
Maltose

Glucoses may be fermented. Add a small quantity of yeast to a test-tube of dilute dextrose or grape-sugar, fit with cork and delivery tube, or simpler, invert in a shallow dish, keep in a warm place—about 25° C.—in about an hour gas, CO_2, is evolved. Collect and

test with lime or baryta water. On boiling after evolution of gas has nearly ceased, alcohol comes off, and may be distinguished by its odour; or it can be oxidised to acetic acid by permanganate and tested for.

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2.$$

CARBON DISULPHIDE, CS_2.—Specific gravity, 1·263. Boiling point, 46·6° C. Refracting power, 1·645.—Disulphide of carbon is a colourless, very mobile, highly refracting liquid, having a peculiarly unpleasant odour. It evaporates quickly at ordinary temperatures, producing great cold. It is almost insoluble in water, but alcohol and ether mix with it in all proportions. It dissolves sulphur, phosphorus, iodine, caoutchouc, oils, and fat, for which purposes it is largely used.

Disulphide of carbon is very inflammable, and burns with a blue flame, producing sulphurous and carbonic anhydrides. A mixture of its vapour and nitric oxide burns with a very bright blue flame, particularly rich in chemically active rays, hence it is sometimes used for photographic purposes.

Dry chlorine converts it in the presence of iodine into tetrachloride of carbon and sulphochloride of carbon, $CSCl_2$. The fixed caustic alkalies gradually dissolve disulphide of carbon, forming a brown solution which is a mixture of carbonate and sulphocarbonate of the alkali metal:

$$3CS_2 + 3K_2O = K_2CO_3 + 2K_2CS_3.$$

An aqueous or alcoholic solution of caustic potash to which a little lead salt, acetate, has been added, boiled with disulphide of carbon, becomes blackened. This is a very delicate test for sulphide of carbon.

With triethylphosphine it unites directly, forming a compound, $P(C_2H_5)_3CS_2$, which crystallises in splendid ruby-coloured prisms, which dissolve in ether with a red colour. This is a good test for CS_2 vapour in other gases.

ALCOHOL, $C_2H_6O = C_2H_5OH$.—Specific gravity, 0·7939 at 15·5°. Boiling point, 78·4° C. at normal pressure.—Alcohol is a transparent, colourless, very mobile liquid, which readily dissolves resins, ethers, fats, essential oils, &c. It mixes with water and ether in all proportions, is very inflammable, burning in the air with a blue flame only very slightly luminous and yielding water and carbonic acid. Its vapour mixed with air explodes by contact with flame or by the electric spark.

When the vapour of alcohol mixed with air comes in contact with platinum black imperfect combustion takes place, the metal being generally heated to redness and the alcohol partly converted into aldehyde, acetic acid, formic acid, acetal, &c.

Strong nitric acid decomposes alcohol, part of the nitric acid forms nitrate of ethyl, but the greater part is reduced to nitrous acid which

then forms nitrite of ethyl, at the same time many other compounds are formed, and the action may become explosive unless the materials are pure and used in small bulk only.

Strong sulphuric acid mixes with alcohol producing considerable evolution of heat with formation of sulphovinic acid. Potassium and sodium act upon alcohol with formation of ethylates and evolution of hydrogen.

$$2C_2H_5OH + K_2 = H_2 + 2C_2H_5OK.$$

The best test for alcohol depends on the production of iodoform, although it is not the only substance which gives this test. It is best performed by warming the liquid to be tested, adding a solution of sodium carbonate, and then small crystals of iodine, until a slight brown coloration remains. On cooling the solution, pale yellow flaky crystals of CHI_3 will fall out. They have a very characteristic odour.

Alcohol may be also very readily oxidised to aldehyde, and then to acetic acid by any oxidising mixture, such as potassium dichromate and sulphuric acid, or potassium permanganate. A liquid containing alcohol when warmed with a strong $K_2Mn_2O_8$ solution, causes a black or brown precipitate of MnO_2 and potassium acetate, which remains in solution, and may be tested for.

ETHER, $C_4H_{10}O = C_2H_5OC_2H_5$.—Specific gravity, 0·736 at 0° C. —Pure ether is a very mobile, colourless liquid, of penetrating odour and sweet taste. On account of its low boiling point, 35° C., it evaporates very rapidly at ordinary temperatures, causing thereby a great reduction of temperature. It mixes in every proportion with absolute alcohol but not with water; 1 part of ether requires about 9 parts of water for solution, and itself dissolves about $\frac{1}{11}$ of its weight of water. It dissolves sulphur, phosphorus, iodine, &c., and is one of the best solvents for fats, oils, resins, and other organic bodies.

It is very inflammable, its vapour mixed with air becoming ignited by platinum black; it burns with a luminous flame; a mixture of its vapour and air is violently explosive.

By incomplete oxidation or imperfect combustion it is converted into aldehyde and acetic acid. It is not attacked by sodium or potassium, but energetically by chlorine. The reaction is most violent with chlorine and its vapour. Bromine acts less violently

Dry ether mixes to a clear liquid with sulphide of carbon; a slight trace of water causes a milkiness.

CHLOROFORM, $CHCl_3$.—Is a colourless liquid, of specific gravity 1·62, boiling at 61° C. It is soluble in about 200 times its weight of water, but to any extent in alcohol, ether, CS_2, &c. It is an excellent solvent for oils and fats, resins, &c.

Chloroform heated with Fehling's alkaline copper tartrate solution produces Cu_2O.

$$CHCl_3 + 5KHO + 2CuO = Cu_2O + K_2CO_3 + 3KCl + 3H_2O.$$

Chloroform vapour passed through a red-hot tube along with

hydrogen liberates HCl. The operation may be performed in an apparatus like Marsh's for AsH_3, the flask being warmed.

Alcoholic soda or potash, warmed with a chloroform solution to which a few drops of aniline have been added, gives benzoisonitrile, C_6H_5NC, a liquid of most penetrating and disagreeable odour.

ACETONE, $\begin{matrix} CH_3 \\ CO \\ CH_3 \end{matrix}$, dimethylketone, is a colourless liquid, obtained on a large scale by the distillation of calcium, barium, strontium, or magnesium acetates. It is contained in very small amount in blood, urine, &c., especially in cases of fever and diabetes. Many organic substances on dry distillation yield acetone amongst other products. It boils at 56·5°. Specific gravity, ·8179 at 0°. It mixes with water, alcohol, ether, chloroform, in almost any proportion. $CaCl_2$ separates it from water. Dehydrating substances act readily on acetone, forming mesitylene oxide, $C_6H_{10}O$, and phorone, $C_9H_{14}O$. H_2SO_4 will form both these bodies.

With NH_4HO and iodine iodoform is produced. Alcohol does not give iodoform with ammonia. Acetone in the presence of KHO dissolves HgO. $HgCl_2$ solution is made strongly alkaline with KHO and then shaken with the supposed acetone solution and filtered. The filtrate will contain Hg if acetone was present. The compound formed is $2(C_3H_6O)3HgO$. A saturated solution of $HNaSO_3$ forms $C_3H_6ONaHSO_3$, with a solution of acetone. It is less soluble in alcohol than water. This is a method of purification of acetone.

Acetone is much used as a solvent for gun-cotton and other nitrated celluloses, in the manufacture of smokeless powders, and for other purposes.

Gun-cotton, $C_6H_7O_2(NO_3)_3$, as made from cotton and a mixture of nitric and sulphuric acids, is fibrous, as is the original cotton or cellulose, but after solution in acetone is left on evaporation of the latter in a horny state, resembling glue.

The term "Normal Salt," frequently used in connection with both organic and mineral acids, means that all the acidic or replaceable hydrogen has been turned out by a metal. They are sometimes neutral to test papers (litmus, &c.), but not always. Some normal alkali salts still react alkaline.

QUALITATIVE ANALYSIS TABLES.

GENERAL REMARKS.

A PRELIMINARY "dry" examination of the substance under analysis should never be omitted before proceeding to the examination for bases in solution.

Apart from the deductions to be drawn from the external properties of the substance, such as its colour, shape, gravity, odour, &c., the detection of certain substances in a preliminary examination will frequently modify the course of analysis to be pursued in solution.

For example, if organic matter has been found by the dry examination, the filtrate from Group II. should be evaporated to dryness, and the residue ignited sufficiently to destroy any such organic bodies as sugar, tartaric or citric acids, which prevent the precipitation of some of the metals in the third group.

But this process of ignition if carried too far renders certain bases insoluble, *e.g.*, Al_2O_3, Fe_2O_3, Cr_2O_3, &c., as well as silica. This would entail a separate analysis of the residue so obtained. If, therefore, the preliminary examination has established the absence of organic matter it is better not to ignite here.

If arsenic has been found in a preliminary examination, the filtrate from Group I. should be boiled with a solution of SO_2 to reduce any pentad arsenic, As_2O_5, compounds, to the state in which it is most easily precipitated by SH_2, viz., As_2O_3.

If double cyanides have been indicated, it is advisable to ascertain whether there are any present that would interfere with the analysis in the ordinary way.

A reasonable economy in the amount of substance used for analysis should always be observed, and sufficient of the original solid or liquid kept to confirm or to correct doubtful results.

The purity of the reagents used is a point that is too often neglected; alumina is often entered in an analysis because the soda used may have contained it, or iron, because fragments of rust from iron apparatus have fallen into the solution. It should also be remembered that ordinary filter paper is not free from impurities, lime, magnesia, iron, &c.; accordingly, where any pretension is made to strict accuracy, paper that has been carefully washed with dilute hydrochloric and nitric acids should be employed.

The term "addition in excess" is frequently misunderstood by beginners.

It should be remembered that after a sufficient quantity of the reagent has been added, any further addition dilutes the solution and may retard the reaction or commence a re-solution or other secondary reaction.

With properly prepared equivalent reagent solutions, equal volumes should complete the reaction in any case, and more is an excess. Generally half as much again may be taken as a fair excess quantity above that actually needed. With what are called normal solutions (see Appendix), say of HCl and NH_3, 1 cc. of each will just neutralise each other, and $1\frac{1}{2}$ cc. of HCl would be an excess of the acid.

When preparing a substance for analysis the smallest possible quantity of acid should be used to bring it into solution (of course

the solution must be left slightly acid in order to separate the second group). The presence of much strong acid necessitates a considerable dilution with water, or a partial neutralisation with ammonia, before the removal of the metals of the second group can be effected; and as the filtrate from Group II. has sometimes to be evaporated to complete dryness before the third group can be analysed, much time is thereby lost.

Even in working through the separate groups, unless care be exercised, the volume of the liquid becomes inconveniently large, and it is no uncommon occurrence to see beginners working with large beakers half full of liquid, whereas the largest vessel used in an ordinary qualitative analysis ought to be a test-tube or a two-ounce flask, or one of the large test-tubes called boiling tubes.

Evaporation between groups is sometimes advisable.

The thorough washing of precipitates in an analysis must be strictly attended to where indicated, particularly between the groups and subdivisions of the groups, or traces of one group may be retained in the precipitate of the preceding one, causing precipitates to appear in the wrong place, or leading to the appearance of small quantities of other substances when such are not actually present. This *must* be attended to; many errors arise from neglect of sufficient washing.

Economy in time may be attained by judicious arrangement of an analysis, as many of the operations can be carried on simultaneously.

Care must be taken to label the tube or vessel the contents of which are not to be proceeded with at once.

The student must use his discretion as to the quantity of the substance or liquid to be taken for the examination of bases in solution, and for this no general rule can be laid down; in bodies or substances where comparatively small quantities of one base are expected to be present with large quantities of another, more of the original substance must be taken; or where the supply at the disposal of the student is large, the trace may be sought for in a separate and larger portion of the original substance, after removal of the bases already detected by the appropriate group-agents.

Heavy precipitates entail much washing, an operation which is tedious but quite indispensable.

Lastly, it is almost unnecessary to remark that strict cleanliness must be observed in all apparatus used for analysis, as there is nothing more annoying than to remember at the end of an analysis, otherwise carefully conducted, in which unexpected results have been obtained, that these may have been due to carelessness in this matter.

All reagent bottles must be replaced immediately after using, and as little loose apparatus permitted on the working bench as possible.

All results, whether positive or negative, must be entered in the note-book *as* obtained, and before passing to the next experiment.

At the end of the exercise the results should always be discussed and the special reactions and tests looked up before making a final report.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY.

The physical properties of a substance under examination, such as its crystalline structure, its odour, colour, hardness, density, are capable of throwing, in many cases, much light upon its composition, and should be carefully noted.

N.B.—*These reactions are given on the supposition that a "single" substance is under examination: they are, however, still true for a mixture, although not so easy to recognise.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.
I. Heat a small portion of the substance, in the state of powder, in a small bulb tube or dry test-tube.	THE SUBSTANCE DOES NOT CHANGE	Absence of organic substances, of volatile inorganic matter, of substances decomposed on ignition, of hygroscopic moisture, of water of crystallisation, of readily fusible matters, and of water of hydration.*
	THE SUBSTANCE CHANGES	
	1. *The substance changes colour*	
	Yellow whilst hot, white on cooling	ZnO.
	From yellow to reddish-brown, whilst hot, yellow when cold, fusible at a red heat	PbO.
	From white to yellowish-brown when hot, dirty, light yellow on cooling	SnO_2. [TiO_2.]
	From white to orange and reddish-brown, dull yellow on cooling, fusible at a red heat . .	Bi_2O_3.
	Dark red whilst hot, reddish-brown on cooling .	Fe_2O_3.
	2. *The substance fuses* and re-solidifies when the flame is removed	Mostly salts of the alkalies, and some salts of the alkaline earths (nitrates, chlorides, &c).
	3. *A sublimate is formed*	Several compounds of ammonium, antimony, mercury, arsenic, also sulphur and iodine (lead chloride sublimes with difficulty). Metallic cadmium, cadmium chloride, volatile organic acids, *e.g.*, oxalic, benzoic, and succinic acids.

	The substance melts at a very gentle heat, heavy fumes appear in the tube, and the sublimate is white and crystalline	$HgCl_2$
	It sublimes without previous fusion, is yellow when hot, white when cold	Hg_2Cl_2.
	The sublimate is black, and turns red on rubbing in the tube or on a paper	HgS.
	The sublimate is yellow	HgI_2, As_2S_3.
	Turns pink on rubbing	HgI_2.
	It consists of reddish-brown drops, yellow when cold	Free sulphur. Sulphides decomposed on ignition.
	The sublimate consists of white octahedral crystals	As_2O_3.
	The substance fuses into a yellow mass, and at a red heat sublimes entirely, forming crystalline needles	Sb_2O_3.
	Violet vapour, feathery bluish-black crystals .	Iodine.
	Odour of frankincense	Benzoic acid.
	Fumes which cause violent coughing . . .	Succinic acid. (Oxalic acid.)
	Heavy white fumes, and white crystalline sublimate	Oxalic acid. $(NH_4)_2CrO_4$ or $(NH_4)_2Cr_2O_7$ burn in a peculiar manner on gently heating, N gas and steam being given off.
Confirm by heating a little of the dry substance with dry Na_2CO_3, or black flux, in a bulb tube.	Metallic mirror and globules of a metal . .	Mercury compounds.
	Black shining mirror, no metallic globules . .	Arsenical compounds.
	Bright metallic mirror and brown ring . . .	Cadmium.
Test also specially for ammonium compounds by grinding a little of the original substance in a mortar with soda-lime, and moistening with water.	NH_3 is given off	Ammonium compounds $(NH_4)_2CO_3$ $(NH_4)_3PO_4$, $(NH_4)_3BO_3$, $(NH_4)_2SO_4$, are decomposed and give off NH_3 when heated by themselves. Alkaline chromates, borates, phosphates, &c., likewise evolve ammonia in the presence of ammonium salts.

* As a matter of fact, if the substance be white and does not change it can only be a compound of Al, Ba, Ca, Sr, Mg and Si with O and a few other substances.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.
	Yellowish and red sublimate, pale green flame at mouth of tube	Phosphorus.
	4. *The substance fuses, and gives off water of hydration* (sometimes without fusion), or water of *crystallisation*, becoming liquid at a low heat, *i.e.*, it fuses in its water of crystallisation, it then solidifies and fuses again when heated more strongly (igneous fusion), and swells up or intumesces considerably	Metallic hydrates and salts containing water of crystallisation, *e.g.*, phosphates, borates, alums, and some others.
Confirm by examining the condensed water with litmus-paper.	Alkaline reaction	Ammonium compounds.
	Acid reaction	Free volatile acids, such as HNO_3, HCl, H_2SO_4, H_2SO_3, &c., or acid salts, organic acids.
	5. *The substance gives off a gas or vapour*	
Confirm by introducing a glowing splinter of wood into the test-tube.	Oxygen is given off, causing a glimmering splinter of wood to burst into flame	Metallic peroxides, chlorates, perchlorates, nitrates, bromates, iodates.
	Oxygen mixed with other gases, *e.g.*, SO_2, N, N_2O_4, Cl, Br, I, is given off	From the decomposition of certain sulphates, of nitrates, nitrites, chlorates, hypochlorites, bromates, iodates.
	SO_2 is given off, recognised by its suffocating odour and its acid reaction with litmus-paper and bleaching of permanganate stain on paper	Acid sulphites; also from the decomposition of sulphates, with or without evolution of oxygen, of earthy sulphites, or thiosulphates; from the action of organic matter upon sulphates, and from the oxidation of metallic sulphides and sulphocyanates.
	Reddish-brown fumes of N_2O_4 come off mixed with oxygen (Action on paper moistened with anaphtylamine sulphate)	Nitrates of heavy metals, *e.g.*, of Pb, Bi, also certain sulphates in presence of an alkaline nitrate.

Confirm by passing the gas through lime or baryta-water.	CO_2 is given off, which is a non-supporter of combustion, and turns lime-water milky	From the decomposition of carbonates (alkaline carbonates excepted); also from the decomposition of oxalates, &c.
	PH_3 is given off, known by its odour; it sometimes inflames; decolorises permanganate	From the decomposition of certain phosphites, hypophosphites, &c.
	C_2N_2 is given off, having a peculiar odour, and burning with peach-blossom-coloured flame	From certain compounds of cyanogen.
	Nitrogen, a non-supporter of combustion; not affecting lime-water	NH_4NO_2, or some fixed nitrite in the presence of ammonium salts (NH_4Cl, &c.), dichromates and ammonium salts.
	ON_2, supporting combustion	NH_4NO_3, or some fixed nitrate in the presence of ammonium salts.
	SH_2, recognised by its odour and action on lead acetate paper	Hydrated sulphides, moist sulphites, and hyposulphites.
	NH_3, possessing a characteristic pungent odour and alkaline reaction to test-paper, litmus or turmeric	From ammonium salts, such as $(NH_4)_2CO_3$, and others containing fixed acids (phosphates, borates); from cyanates in the presence of water, and from the decomposition of organic substances containing nitrogen, accompanied by carbonisation and evolution of offensive smelling substances.
	CS_2 is given off	From the decomposition of sulphocyanates.
	Cl is given off, recognised by its pungent odour. The gas bleaches moistened litmus-paper	Several chlorides, such as those of the noble metals Pt, Au; also from certain chlorates and hypochlorites.
	Br and I are given off, recognised by the colour of their vapour, or sublimate, and their action on starch paste	Several bromides and iodides when heated by themselves with exclusion of air, or in the presence of air; in the latter case with formation of oxides, also some bromates and iodates.
	Sulphur vapour, which condenses in the upper part of the tube in yellow drops, and burns with a blue flame	From the decomposition of metallic persulphides, *e.g.*, PtS_2, Au_2S_3, Sb_2S_5, SnS_2, FeS_2, which leave either a lower sulphide or the metal.
	6. *The substance becomes carbonised and evolves strongly odorous products of decomposition*	From the decomposition of organic animal substances.

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.
	Acetone *evolved*. It has an aromatic odour somewhat like ginger	From the decomposition of acetates.
	A carbonate is left which effervesces with dilute acids, whilst the original substance does not effervesce	Organic acids, combined with alkaline, or alkaline earthy bases.
	The carbonate in the residue is soluble in water, and shows an alkaline reaction	Organic compounds of the fixed alkali metals.
	The carbonate is insoluble in water . . .	Organic acids, combined with other than the alkaline metals.
II. Heat a little of the substance under examination on charcoal before the blowpipe flame.	**1.** *The substance decrepitates*	NaCl and other crystalline salts.
	Prevent decrepitation by fine powdering or moistening it with water	
	2. *The charcoal burns violently, deflagration*	Nitrates, chlorates, &c.
	3. *The substance fuses readily, and sinks into the charcoal or forms a liquid bead*	Salts of alkalies, and some salts of alkaline earths, and a few chlorides and bromides.
	4. *An infusible residue is left*	
	(a) *The residue is white* and highly luminous .	BaO, SrO, CaO, MgO, Al_2O_3, ZnO, also SiO_2, and especially some of the rare earths, as ZrO_2, ThO_2.
	Alkaline to test paper	BaO, SrO, CaO, MgO.
	(b) *The residue is coloured*	Cu, Co, Ni, Mn, Fe, Cr, and some of the rare metals.
Confirm by heating a small quantity of the residue in a clear **borax** bead on a platinum wire, in the inner and outer blowpipe flames.	Oxidising flame: green bead whilst hot, blue when cold. Reducing flame: red bead when cold	Cu.

Graphite, and some other forms of carbon, and some of the platinum metals will remain unchanged.

	Sapphire blue bead both in the oxidising and reducing flame	Co.
	Hyacinth-red to violet-brown bead when hot, yellowish to sherry-red when cold	Ni.
Confirm the presence of Mn also by fusion with nitre and Na_2CO_3 on platinum foil. (See Mn.)	Amethyst-red bead in oxidising flame. Colourless bead in reducing flame	Mn.
	Brownish-red bead when hot, light yellow, or colourless when cold in the oxidising flame; an olive-green to bottle-green bead in the reducing flame	Fe.
Confirm the presence of Cr by fusion with nitre and *fusion mixture* on platinum foil. (See Cr.)	Green both in oxidising flame, and in reducing flame	Cr.
Heat a portion of the infusible residue in a bead of microcosmic salt	The hot bead is colourless, and remains clear on cooling	Sb, Al, Zn, Cd, Pb, Ca, Mg.
	It becomes enamel-white on cooling, although a small amount only has been used	BaO, SrO.
	The substance dissolves slowly and particles float about in the bead as a silica skeleton	SiO_2.
	5. *The substance is reduced to the metallic state, but no bead is obtained; the metal is volatile, and on passing through the outer flame yields an* **incrustation**	
	A white incrustation and characteristic garlic-like odour	As.
	Incrustation yellow when hot, white when cold	Zn.
	Incrustation reddish-brown (readily volatilised)	Cd.
	6. *The substance is reduced to the metallic state, and shows indications of the production of a bead*	Au, Ag, Cu, Pb, Sn, Bi, Sb, *Cd.*

PRELIMINARY EXAMINATION OF SOLIDS IN THE DRY WAY—*continued.*

EXPERIMENT.	OBSERVATIONS.	INFERENCE.
Confirm by mixing a little of the substance with Na_2CO_3 and KCy, and heating on charcoal in the inner blowpipe flame.	(A). *A metallic bead is produced without noticeable incrustation*	
	Brilliant white metal	Ag.
	Yellow metal	Au.
	Red scales or globules of a red metal, showing better on rubbing	Cu.
	(B). *With incrustation*	Sn. Pb. Bi, Sb, Cd.
	Metal malleable ; *slight incrustation*, which is yellow when hot, white when cold . . .	Sn.
	Metal brittle ; incrustation dark orange when hot, lemon-yellow when cold	Bi.
	Metal malleable ; marks paper ; incrustation lemon-yellow whilst hot, yellow when cold .	Pb.
	Metal brittle ; gives off white fumes when withdrawn from the flame, and becomes surrounded with a network of brilliant acicular crystals of Sb_2O_3 ; incrustation white, and *close to the substance*	Antimony compounds.
	Small scattered metallic globules, soft ; fine brown incrustation	Cadmium.
Heat a little of the substance mixed with dry Na_2CO_3 (free from sulphate) in the reducing flame ; place the fused mass on a bright silver coin and moisten it with water.	The silver is stained black, and the fused mass evolves SH_2, when treated with dilute HCl	Presence of sulphur, either free or in combination.

III. Heat in the inner blow-pipe flame, or in the lower outer edge of a non-luminous flame, on a clean platinum wire. **This test may with advantage be applied earlier than here indicated.**	**1.** *The substance colours the flame* Golden yellow . . . . Violet . . . . Yellowish-green . . . . Crimson . . . . Reddish . . . . Green . . . . Blue	Na compounds. K ,, Ba ,, Sr and Li compounds. Ca ,, Cu, B_2O_3. As, Sb, Pb, $CuCl_2$, $SnCl_2$, $MnCl_2$, $NiCl_2$, and some others also give green or blue-green flames.

Note 1.—**A few of the changes observed on heating a substance** by itself in a bulb tube **occur again when** the substance is heated **on charcoal, but may be neglected,** as they are more readily studied in the tube.

Note 2.—**A substance under examination** may consist of several bodies, and the reactions which it gives may frequently obscure each other. **Moreover, Analytical** Tables cannot possibly provide an explanation for every change that may be produced during the **preliminary examination of a** mixture of several substances. The student should, therefore, record faithfully every observation he **makes, though he may not be able** at the time to draw an inference from it, and should endeavour to elicit by furthur experiments **what** substances are present in the mixture which he is called upon to examine. Everything should be written down *as soon* as **performed. The tabular** form here employed is perhaps the shortest and clearest for the purpose. The evidence for and against **must then be balanced up.**

Note 3.—**Graphite and** some gas carbons **will pass** through all **these** trials without change, as also will some of the platinum group **of metals.**

EXAMINATION OF A SUBSTANCE IN SOLUTION.

1st. *The substance under examination may be a liquid.*—Examine it by means of well prepared test papers. The liquid may be **neutral**.—This excludes a large number of substances, since the greater proportion of normal salts of the metals possess an acid reaction.—The liquid gives an **acid** reaction. This may arise from a free acid, or from the presence of a normal salt having an acid reaction, or from an acid salt.

The solution possesses an **alkaline** reaction—showing the presence of a salt of alkaline reaction, of free alkalies, or alkaline earths, and of cyanides or sulphides of the alkalies or alkaline earthy metals.

Evaporate a portion of the liquid to dryness, on a watch-glass, or platinum foil. If it leave no residue it may consist of pure water only, or of a solution of some substance which evaporates along with the water or other solvent; if it leave a residue a larger portion of the liquid should then be evaporated to dryness in a porcelain dish and subjected to a preliminary examination in the dry way.

2nd. *The substance under examination may be a solid.*—If it occur in large pieces, or in the form of a coarse powder, it should first be reduced by mechanical means to as fine a powder as possible.

Natural silicates and compounds which are decomposed with difficulty by acids, are finely powdered in an agate mortar and, if necessary, sifted. The coarse particles must then be ground again till the whole of the substance is obtained in an equally fine state of division.

Ascertain whether the solid substance is wholly or in part soluble in water. This is done by boiling about a gramme of it in distilled water, allowing the undissolved portion to subside, and evaporating a few drops of the water to dryness on a watch-glass.

The residue insoluble in water is next treated with dilute hydrochloric acid, and heated for some time to boiling.

If the substance is not completely dissolved by these means, it is best to take a fresh quantity in a test-tube, pour over it two or three cubic centimetres of concentrated hydrochloric acid, and then to boil until half the acid has evaporated away. Water is added, the contents of the tube are warmed, and if a residue remains it may be treated again in the same way. What fails to dissolve by this method should be regarded as insoluble unless the residue is known by its appearance, or by the preliminary examination, to contain something that would dissolve in aqua regia. In this case, treat the residue with aqua regia, boil off the acids, and add the solution to the hydrochloric solution. Nitric acid or aqua regia should never be used unless it is certainly known that they will be advantageous, *e.g.*, with metals.

The residue insoluble in water and acids should be carefully washed with distilled water, dried, and then mixed with four times

its weight of dry Na_2CO_3 and K_2CO_3 (fusion mixture) and fused. The fusion is best performed in a platinum vessel provided the insoluble residue contains no metals capable of forming alloys with platinum. This can be readily ascertained by an examination of a portion of the residue in the dry way.

It should be borne in mind that only barium and strontium sulphates; silver chloride; SiO_2, and many silicates; native or ignited Al_2O_3 and aluminates; ignited Cr_2O_3 and Fe_2O_3; chrome iron ore; SnO_2 (ignited or as tinstone); ignited Sb_2O_4 (a few metaphosphates and arsenates); CaF_2, and a few other native fluorides; sulphur and carbon, as charcoal or graphites, can be present in the insoluble residue.

Silver compounds in general are changed into AgCl by boiling with aqua regia, and AgCl can be easily removed from an insoluble residue by means of ammonium hydrate.

The examination of a residue requiring fusion with alkaline carbonates is invariably conducted separately. The fused mass is boiled with water and filtered; the part insoluble in water containing the base in the form of a carbonate (oxide or metal) is dissolved in HCl. The aqueous extract is examined for such acids as would form insoluble compounds with the bases found as well as for silica.

Alloys should be examined in the dry way as well as the wet way. Alloys are dissolved in dilute or concentrated HCl, sometimes with the aid of platinum foil, or in a platinum basin, or with the addition of a few crystals of potassium chlorate, but in this case NOT in a platinum vessel, and their solutions examined as usual.

Cyanogen compounds are treated of after the tables for the separation of the metals.

As they can all be decomposed by heating to redness in an open dish the metals previously in combination can be sought for in this ignited residue.

N.B.

REFER TO THESE "NOTES" TO GENERAL TABLE.

(*See reference numbers in table.*)

1. If chromium has been indicated in the preliminary examination, and the solution or substance has a yellow or orange colour, make a fresh solution by boiling with a little concentrated HCl and diluting, whether the substance is soluble in water alone or not.

2. If cyanogen has been detected in the preliminary examination, it is advisable to test a portion of the original substance for double cyanides before proceeding in the usual way.

3. If iodine or bromine is present, the solution or substance should be boiled with aqua regia until it is eliminated before passing on to Group II.

4. If the original substance had to be dissolved in HCl, SH_2 may be passed at once.

5. In a saturated solution of a barium or sodium salt, HCl produces a white precipitate which may redissolve in hot water. Such precipitates, however, are never produced in a properly prepared solution. From an alkaline solution HCl may precipitate $Si(HO)_4$ (gelatinous), *benzoic and uric acids* (*crystalline*), *also* Sb_2O_5 (amorphous). Metallic oxides, such as Al_2O_3, and metallic sulphides, such as As_2S_3, Sb_2S_5, Sb_2S_3, SnS, and SnS_2, which dissolve in soda or ammonia, or ammonium sulphide, may likewise be precipitated on the addition of HCl to a solution that is alkaline, and are best examined separately.

6. Oxychlorides of Bi, Sb, or Sn may be precipitated on the first addition of dilute HCl or water, but are readily redissolved on the addition of more acid and gently heating, or the precipitate may be disregarded if the metals of Group I. are absent, since SH_2 readily converts the finely divided oxychlorides into the corresponding metallic sulphides.

7. If arsenic has been detected in the preliminary examination, this filtrate which may contain pentad arsenic, should be boiled with a solution of sulphurous acid, and the acid solution evaporated considerably to expel the SO_2. Ba, Sr, Pb, when present, may be precipitated either partly or wholly as sulphates. The precipitate is best examined separately.

8. SH_2 often produces merely a precipitation of sulphur, owing to the presence of oxidising agents such as Cl, Br, I, H_2SO_3, HNO_2, HNO_3, ClHO, $HClO_3$, H_2CrO_4, or ferric salts. This precipitate is easily distinguished by its being white and remaining suspended in the solution. It may be filtered off and neglected. A brick-red precipitate of Pb_2SCl_2 often comes down from strongly acid solutions if they have not been sufficiently diluted with water. Cadmium is very often left in solution if *too much acid* is present.

9. SH_2 should be passed once more through the filtrate to make sure of the complete precipitation of all the metals of Group II., and it is advisable to dilute a few drops with four or five times their volume of water and pass SH_2. If this further dilution enables SH_2 to give more precipitate, the whole solution must be so treated.

10. It is possible that this SiO_2 may be mixed with other substances, *e.g.*, Al_2O_3, Cr_2O_3, Fe_2O_3 (rendered insoluble by strong ignition), $BaSO_4$, $SrSO_4$, in which case it is necessary to examine it separately.

11. Small quantities of borates and fluorides of the alkaline earthy metals may likewise be precipitated, but need not be examined further, since their bases will be detected in Group IV., and their acids on examining in the usual way for acids.

12. The solution must not be boiled, since the NH_4Cl by double decomposition dissolves the alkaline earthy carbonates, forming chlorides of the metals and ammonium carbonate which volatilises with the aqueous vapour.

AGRICULTURAL COLLEGE

EXAMINATION OF A SOLUTION FOR COMMON BASES.

A Simple General Table for Separation of the Groups.

Do not omit to refer to "Notes" to General Table on p. 221.

Notes 1, 2, 3. To the solution add HCl, as long as a precipitate is produced, and cool the solution if crystals of $PbCl_2$ appear (Note 4).

<table>
<tr>
<td rowspan="5">The PRECIPITATE may contain—
$PbCl_2$
$AgCl$
Hg_2Cl_2
(Notes 5 and 6)

Examine by Table I.</td>
<td colspan="5">The FILTRATE (Note 7) is saturated with gaseous SH_2, and gently heated (Notes 8 and 9).</td>
</tr>
<tr>
<td rowspan="4">The PRECIPITATE may contain—
Hg
Pb
Bi
Cu
Cd
Sn″
Sn^{iv}
Sb‴
Sb^{v}
As
Au
Pt
As hydrated sulphides.</td>
<td colspan="4">Evaporate the FILTRATE till free from SH_2, then add a few drops of concentrated HNO_3 and boil again. If soluble silicates are suspected evaporate to dryness. If organic matter is present, evaporate to dryness and ignite to destroy it. Moisten the residue in either case with strong HCl, add H_2O, heat and filter off the SiO_2 (Note 10), or the carbonaceous matter. Test two or three drops of the solution with an equal bulk of strong HNO_3, and about six times its bulk of $(NH_4)_2MoO_4$, with gentle warming. A yellow precipitate shows the presence of phosphoric acid.
To the solution, prepared as may be necessary, add a considerable quantity of NH_4Cl, boil for a few seconds, add NH_4OH, until after boiling up the smell of it is persistent, and filter at once.</td>
</tr>
<tr>
<td rowspan="3">The PRECIPITATE may contain—
$Fe_2(OH)_6$
$Cr_2(OH)_6$ Hydrates.
$Al_2(OH)_6$
And also phosphates of Groups 3, 4 and Mg, if they are present. (Note 11.)

Examine by Table IIIA or IIIc.</td>
<td colspan="3">Pass SH_2 through the FILTRATE, and warm.</td>
</tr>
<tr>
<td rowspan="2">The PRECIPITATE may contain—
ZnS
MnS
NiS
CoS
As hydrated sulphides.

Examine by Table IIIB.</td>
<td colspan="2">To the FILTRATE add NH_4OH unless it already smells of ammonia, then add $(NH_4)_2CO_3$, and warm gently (Note 12).</td>
</tr>
<tr>
<td>The PRECIPITATE may contain—
Ba
Sr As carbonates.
Ca

Examine by Table IV.</td>
<td>The FILTRATE may contain—
$MgCl_2$
KCl (Chlorides.)
NaCl

Examine by Table V.</td>
</tr>
</table>

Table I.—SEPARATION OF THE

Attend to the Fo

Precipitate may contain $PbCl_2$, AgCl, Hg_2Cl_2 (Note 1. Ge

The SOLUTION may contain $PbCl_2$. On cooling white acicular crystals fall out. Confirm by adding solution of K_2CrO_4. A yellow precipitate indicates PRESENCE OF Pb.*	The white RESIDUE may con The SOLUTION may contain AgCl with HNO_3. A white curdy precipitate indica PRESENCE OF Ag.*

Table II.—SEPARATION OF THE ME

The precipitate may contain HgS, PbS, Bi_2S_3, CuS, CdS, SnS, SnS_2, Sb_2S_3, Sb_2S_5, the precipitate until free from HCl; boil with sod

RESIDUE.—Wash well; boil in a little HNO_3, diluted with an equal bulk of wat action ceases. Dilute with water; add dilute H_2SO_4, as long as a precipit duced; cool, add an equal bulk of alcohol (methylated); filter (F.N. 2).

RESIDUE.—May contain HgS, $PbSO_4$, and S. Boil in ammonium acetate or HCl: $PbSO_4$ dissolves; allow to cool and filter.		SOLUTION.—Boil off the alcohol, add NH_4OH; boil and filter.		
RESIDUE consists of HgS and S or of S only. To confirm, dissolve the black residue in a little aqua-regia, boil off free chlorine, neutralise with NaHO, acidify with HCl, and introduce a strip of bright metallic copper into the solution. It becomes white or silvered. INDICATES PRESENCE OF Hg.*	SOLUTION.—Add K_2CrO_4, yellow precipitate of $PbCrO_4$ indicates PRESENCE OF Pb.*	The PRECIPITATE consists of $Bi(HO)_3$. Dissolve in a few drops of dilute HCl and pour the solution into 250 or 300 cc. water. A white precipitate of BiOCl indicates PRESENCE OF Bi.*	The solution, divide int i. If blue, add KCy till colourless and pass SH_2. A yellow precipitate of CdS INDICATES PRESENCE OF Cd.*	Blue cat ac aci K_4 rec pr Cu INDI SEN

F.N. 1.—CuS is somewhat soluble in $(NH_4)_2S$ and HgS in SNa_2. It is therefore If both CuS and HgS are present dissolve in $(NH_4)_2S$, when a little CuS w

F.N. 2.—Do not add the H_2SO_4 and alcohol unless they are shown to be r

F.N. 3.—Separation of Sb and Sn. Neutralise the cold HCl solution of the t Sb is precipitated. Filter. Solution contains the Sn. Add a little HCl, a

GROUP I. (Precipitated by HCl.)
tions accurately.

precipitate on filter with hot water till quite free from $PbCl_2$.

l_2; heat gently with excess of dilute NH_4OH.

RESIDUE is black, consisting of NH_2HgCl. Dissolve in a little aqua regia, nearly neutralise, test solution with a strip of bright metallic copper. per becomes covered with a grey deposit, which omes silvery when rubbed. Indicates

PRESENCE OF Hg.*

CAUTION.—Unless HCl be added i cess, and the solution gently he oxychlorides of Bi, Sb, as well (likewise H_4SiO_4 indicated by formation of a jelly or gelat precipitate) and a few other stances may become precipitat this group.

UP II. (Precipitated by SH_2 in an acid solution.)

t must be tested for specially in a separate portion of the filtrate from Group I.) monium sulphide, or sodium sulphide, and filter (F.N. 1).

TION may contain As, Sb, Sn (Au and Pt) as sulpho-salts. Acidulate with dilute S_3, Sb_2S_3, and SnS_2 are re-precipitated. Filter and wash; boil with a little concent l until SH_2 ceases to be evolved, add equal bulk H_2O and filter.

TION. F.N. 3. Pour into a porcelain dish and put into piece of platinum foil with a strip of zinc in contact h it.

k stain on the platinum face indicates the

PRESENCE OF Sb.*

Allow the zinc to remain until the acid is exhausted, scrape the deposit off the zinc that it may be removed clean, and dissolve the precipitated metal in a little strong HCl in contact with a piece of platinum, and add $HgCl_2$ to the solution. A white precipitate of Hg_2Cl_2 or a grey precipitate of Hg indicates the

PRESENCE OF Sn.*

RESIDUE contains the or only sulphur.
Confirm As by heating dried residue with KC Na_2CO_3 in a bulb tube. if $(NH_4)_2S$ has been us that there is much su in this residue, the may be dissolved in a aqua regia and Rei test applied. That is wa with clean metallic c in a test tube. A grey ing indicates As. This ed Cu when heated dry test-tube should white crystalline subl of As_2O_3.*

ve the precipitate in the absence of CuS with $(NH_4)_2S$, and in the absence of HgS with solution.
a precipitate with a few drops of the solution.
NH_4OH; add an excess of a strong solution of oxalic acid, pass SH_2 till the whole me time. Brown or yellow precipitate. Presence of Sn.

TABLE IIIA.—SEPARATION OF THE METALS OF GROUP IIIA.

(In the absence of Phosphates.)

<table>
<tr><td colspan="3">The PRECIPITATE consists of $Fe_2(HO)_6$, $Cr_2(HO)_6$, and $Al_2(HO)_6$, precipitated by NH_4OH in the presence of NH_4Cl. Wash with hot water. Dissolve in dilute HCl, add a solution of NaHO in excess, and boil for some time. Filter off.</td></tr>
<tr><td colspan="2">RESIDUE insoluble.—Dry and fuse with fusion mixture and nitre on platinum foil. Boil in water, and filter.</td><td rowspan="2">SOLUTION. — Acidulate with dilute HCl, and add NH_4OH in slight excess, or solid NH_4Cl may be added, and the solution boiled.
White gelatinous precipitate indicates

PRESENCE OF Al.

Note.—If no sodium hydrate free from alumina can be obtained, it should be made by dissolving a little sodium in alcohol, adding water and evaporating in a silver or platinum dish until the alcohol has evaporated. Failing silver or platinum, a nickel dish is quite safe.</td></tr>
<tr><td>RESIDUE. — Dissolve in dilute HCl, and add K_4FeCy_6.
A precipitate of Prussian blue indicates

PRESENCE OF Fe.

Test the original HCl solution specially for ferrous and ferric iron by means of K_4FeCy_6, $K_6Fe_2Cy_{12}$, or NH_4SCN.</td><td>SOLUTION yellow. Confirm by adding acetic acid and lead acetate.
Yellow precipitate of $PbCrO_4$.

PRESENCE OF Cr.

Note.—Traces of manganese—owing to imperfect separation of Mn from Fe by precipitation with NH_4OH and NH_4Cl—are indicated by the bluish-green colour of the fused mass arising from the formation of an alkaline manganate.</td></tr>
</table>

TABLE IIIB.—SEPARATION OF THE METALS OF GROUP IIIB.

(In the absence of Phosphates.)

The PRECIPITATE may consist of ZnS, MnS, NiS, CoS.* Wash off the filter and dissolve the precipitate in dilute HCl, with the addition of a small crystal or two of $KClO_3$ if the precipitate is black. Boil, add NaHO in excess, boil, and filter, after allowing to cool a short time.†

I. The SOLUTION may contain Zn, as $Zn(NaO)_2$. Add SH_2. White precipitate of ZnS indicates

PRESENCE OF Zn.§

II. The INSOLUBLE RESIDUE *may contain* $Mn(HO)_2$, $Co(HO)_2$, and $Ni(HO)_2$. Wash, dissolve in a little HCl; nearly neutralise with NH_4OH; add excess of ammonium acetate; pass a rapid current of SH_2 for several minutes through the solution and filter. The solution should be acid with acetic acid.

II a. The SOLUTION *contains* the manganese as acetate.
Add NH_4Cl, NH_4OH and SH_2, or ammonium sulphide direct to the solution.
Flesh - coloured precipitate of MnS indicates

PRESENCE OF Mn.§

II b. RESIDUE.—Dissolve in HCl and $KClO_3$; *thoroughly* expel SH_2; nearly neutralise with solid Na_2CO_3; add a solution of KCy, so as just to redissolve the precipitate first produced. Boil briskly for a few minutes, allow to cool (filter off any slight precipitate), and add an equal bulk or more of a strong solution of NaOCl;‡ warm gently as long as a black precipitate forms, and filter.

II b 1. PRECIPITATE consists of $Ni_2(HO)_6$. Filter off and confirm by heating a small portion of it on a borax bead before the blowpipe flame.
A *yellowish to* sherry-red bead indicates

PRESENCE OF Ni.§

II b 2. The SOLUTION contains the cobalt as $K_6Co_2Cy_{12}$. Evaporate a small part to dryness, and test the residue before the blowpipe flame on *a borax bead*.
A blue bead in *both flames* indicates

PRESENCE OF Co.§

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* Unless this precipitate is black no Ni or Co need be looked for.

† Boiling alkaline solutions are liable to disintegrate the paper of the filter.

‡ Strong bromine water with NaOH may be used instead of NaOCl. A bleaching powder solution may also be used. Also chlorine water.

§ The precipitates should be saved for final confirmatory tests.

It is well for the student to have a known mixture given for examination containing a few metals, and to be required to separate and confirm not only by these plans, but to be required to construct modified plans of analysis based on the reactions of the metals given in chaps. ii.–vi.

It will have been noted that no place has been found in the separation tables for some of the non-metallic substances, as carbon, sulphur, phosphorus, &c. These bodies are easily found in the preliminary dry examination.

EXAMINATION FOR ACIDS. CAUTIONS.

Before proceeding to the examination for acids, the student will do well to consider carefully which acids can possibly be combined with the bases present. A perusal of the Table of Solubility of Salts, given in the Appendix, will materially aid him, and will probably save much labour and time. Some acids are detected on examining for bases viz., As_2O_3, As_2O_5, SiO_2 and H_3PO_4 in combination with metals of Groups III. and IV.; H_2CrO_4, CO_2, SH_2, H_2SO_3, $H_2S_2O_3$, ClHO, HNO_2, the six lastly mentioned acids on dissolving the substance in dilute HCl, or on adding HCl in Group I. The student should be on the look out for them.

A careful preliminary examination for acids will probably lead to the detection of a further number of acids, *e.g.*, of HI, HIO_3, HBr, $HBrO_3$, and $HClO_3$, HNO_3, HNO_2, HCl, ClHO, HF, HCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$, CyOH, and CySH, acetic, oxalic, and other organic acids, may likewise be indicated. When more than one of these acids is present, the detection is somewhat more difficult, and the results obtained by a preliminary examination for acids require to be carefully confirmed by the examination of the solution.

Thus, a chloride in the presence of a nitrate, when treated with concentrated H_2SO_4, evolves chlorine and red fumes of lower oxides of nitrogen, and possibly nitrosyl chloride; in the presence of a chromate brownish-red fumes of CrO_2Cl_2.

When the preliminary examination gives no distinct indication of the presence of any of the acids just mentioned, H_2SO_4, $B(HO)_3$, H_3PO_4, SiO_2 must be looked for specially. A fluoride with an excess of a borate *does not etch glass*. The student must bear in mind that acids cannot be detected in quite the same systematic order as bases, and that he ought therefore never to be satisfied till he has confirmed the presence of acids by the most characteristic special tests.

At the same time there is a natural or logical order of procedure in the case of acids, and the student is strongly urged to study and construct plans of separation and detection of mixed acids. It will be found an extremely valuable exercise.

Remember that in this preliminary examination table the inferences are, in most cases, "indicate" only, not absolute proofs.

Other tests should be applied, and if the student has done *some* of the *experiments* under the headings of each of these acids, &c., confirmatory tests will immediately suggest themselves.

PRELIMINARY EXAMINATION FOR ACIDS.

Experiment.	Observation.	Inference.
I. Treat a little of the powdered substance in a test-tube with dilute HCl, and warm gently.	Certain acids are given off as gas or vapours— **1.** Without decomposition A colourless and inodorous gas is evolved with effervescence, which precipitates baryta-water. (Metallic Al, Fe, Mg, Zn, Ni, Sn, liberate hydrogen with effervescence.) The evolution of H by the action of HCl or H_2SO_4 is a certain indication of a metal	CO_2 from carbonates, likewise from cyanides and cyanates containing carbonates.
	A gas is evolved having the odour of burning sulphur	SO_2 from sulphites.
	A gas is given off possessing a fetid odour—like rotten eggs	SH_2 from metallic sulphides.
	Reddish-brown fumes	N_2O_3 from nitrites.
	A colourless gas, possessing the odour of bitter almonds	HCy from cyanides.
	2. With decomposition A yellowish-green gas of suffocating odour, bleaching vegetable colours, as litmus	Cl from hypochlorites; also from decomposition of H_2CrO_4 or $K_2Mn_2O_8$ by the HCl.
	SO_2 is evolved and yellow sulphur is precipitated .	From thiosulphates.
II. Treat a little of the substance with concentrated H_2SO_4, and warm (not sufficiently, however, to volatilise the H_2SO_4). Care must be taken about this.	Certain acids are given off— **1.** Without decomposition	HNO_3, HCl, HCy, HF, benzoic, succinic, acetic.

PRELIMINARY EXAMINATION FOR ACIDS—*continued.*

Experiment.	Observation.	Inference.
Distinguish HCl by heating with MnO_2 and H_2SO_4.	Cl gas is evolved, recognised by its odour and bleaching moist litmus paper	HCl.
Distinguish HF by etching on glass or by heating a portion of the original substance with silica and strong H_2SO_4, and holding a wet glass rod in the fumes produced in the tube.	The drop of water on the rod is encrusted over from precipitation of SiO_2 upon it	HF.
Confirm HNO_3 by adding concentrated H_2SO_4 to a portion of the salt and steadily pouring on a solution of $FeSO_4$ in a test-tube or adding crystals of $FeSO_4$, $6H_2O$, and then H_2SO_4.	A brown ring is formed	HNO_3.
	2. With decomposition	ClHO and CyOH (already noticed), SH_2, HI, HBr, $ClHO_3$, $HBrO_3$, H_2CrO_4, formic, tartaric, citric, oxalic, CySH, H_4FeCy_6, $H_6Fe_2Cy_{12}$.
	SH_2 as well as SO_2 are evolved owing to the action of reducing agents upon H_2SO_4	Metallic sulphides, &c.
	Oxygen is given off, and the yellow chromate is changed into green chromic sulphate	H_2CrO_4.
	Chloric peroxide, a greenish-yellow, highly explosive gas is given off	$HClO_3$
	Bromine is evolved (together with HBr and SO_2), which condenses to a reddish-brown liquid ; the gas colours starch paste yellow	HBr and $HBrO_3$.
	Iodine is given off; violet fumes and sublimate, colouring starch paste blue	HI.
	Chlorine is evolved	HCl in the presence of chromates or $K_2Mn_2O_8$, MnO_2, &c.
	Chlorine and nitrous fumes are given off . . .	HCl together with HNO_3 or HNO_2.
	CO is given off without blackening	Formic acid.

	The substance blackens, owing to separation of carbon, with evolution of CO, CO_2, and SO_2, and gives off the characteristic odour of burnt sugar	Tartaric and citric acids.
Confirm oxalic acid by treating a portion of the original substance with MnO_2 and dilute H_2SO_4. If a carbonate is present, it must first be decomposed with dilute H_2SO_4, and then treated as above. (See Oxalic Acid.)	CO and CO_2 are evolved without blackening . .	Oxalic acid.
	The acid is decomposed into CO and NH_3, the latter remaining combined with the H_2SO_4	Cyanides, ferro- and ferri-cyanides.
	CO_2 is given off, and ammonium sulphate is left	Cyanates.
	CO_2 and SH_2 are evolved with separation of sulphur, which reacts upon the H_2SO_4, and forms SO_2, ammonium sulphate being left	Sulphocyanates.
	No gas or vapour is evolved	SiO_2, HPO_3, H_3PO_4, H_2SO_4, H_3AsO_4, HIO_3.

EXAMINATION OF SOLUTION FOR ACIDS.

Before proceeding to this part of the systematic analysis, it is imperative that the student shall carefully consider what acids it is necessary to look for. Some have, perhaps, been indicated as probably present, and there may be other acids that cannot have revealed themselves because of the presence of some interfering constituent. For instance, HCl cannot show in the preliminary examination if HBr is present, because the latter acid gives all the indications that HCl can give. Again, there are a few acids, like H_2SO_4, that give no, or few, preliminary indications of their presence; they must, therefore, always be looked for if it is possible for them to be present.

Having made a list of the acids that are to be searched for, the next matter for consideration is the method of pursuing the search, particularly the preparation of a suitable solution for each test. The practice of *always* preparing the solutions by first boiling with sodium carbonate is not to be recommended.

If the bases present do not interfere, each solution should be prepared by adding the required acid to the aqueous solution, or to the solid substance itself, filtering if necessary. No bases interfere in looking for H_2SO_4 or HCl in a solution.

If bases have to be got rid of (as for instance Pb in preparing a solution to test for H_2CrO_4, Ca, in a solution for oxalic acid), the solid substance is boiled with a slight excess of Na_2CO_3 solution, the precipitate is filtered off, and those solutions that may happen to be required are prepared in the following way from the filtrate:*—

1. Dilute HCl is added to a portion of it, as long as CO_2 is evolved, and till the solution is rendered distinctly acid.
2. Another portion of the alkaline filtrate is rendered acid by means of dilute HNO_3 and boiling.
3. A third portion is rendered acid by means of dilute acetic acid.
4. A fourth portion is carefully neutralised by first adding dilute HNO_3, drop by drop, and boiling as long as CO_2 or other volatile acid is evolved, and till the solution is distinctly acid to test-paper; then by adding a few drops of very dilute ammonia hydrate till the solution gives a neutral reaction with blue and red litmus-papers. The *strictest attention must be paid to these directions*, and the least possible excess of either acid or alkali should be employed, since the precipitation of several acids is prevented by the formation of an ammonium salt in anything like large quantities, on account of the formation of a soluble double salt, *e.g.*, ammonium calcium tartrate, ammonium calcium citrate, &c.

* If a metal is present that must be got rid of, but which Na_2CO_3 will not precipitate, it will be necessary to precipitate it as sulphide from a slightly acid solution. Hg in presence of HCy, Cu, and Sb, in presence of tartaric acid, &c., are examples requiring this treatment.

If the preliminary examination for bases has shown the presence of ammonium salts, it may be necessary to decompose them by boiling with NaHO solution before preparing Solution 4.

Ebullition or fusion with Na_2Co_3 decomposes the phosphates of the alkaline earths but imperfectly; the phosphoric acid so combined is, however, invariably detected by means of ammonium molybdate.

No further notice need be taken of the following acids: CO_2, SH_2, SO_2, HNO_2, ClHO, HCy, since they are detected with certainty in the preliminary examination.

1. HCl Solution.

If present:

H_2SO_4.—On adding solution of $BaCl_2$, a white precipitate, insoluble on boiling.

$2HF,SiF_4$.—On the addition of $BaCl_2$, a gelatinous translucent precipitate of BaF_2SiF_4 is obtained. Confirm by drying and heating the precipitate in a tube, when SiF_4 is given off. Take the residue and heat with Na_2CO_3 on charcoal, place fused mass on silver coin and add 1 drop HCl, brown stain indicates S as H_2SO_4. NH_4OH produces in some solutions gelatinous H_4SiO_4, with formation of NH_4F, BaF_2, and OH_2.

To filtrate, or another portion, or same solution if no result from $BaCl_2$ add Fe_2Cl_6.

H_4FeCy_6.—A deep blue precipitate.

$H_6Fe_2Cy_{12}$.—A brown coloration only. If both acids are present, after adding a slight excess of Fe_2Cl_6, boil and filter off, and observe the colour of the filtrate. If on the addition of SO_2 or $FeSO_4$ to the filtrate, a blue precipitate is obtained, it is confirmatory of the presence of $H_6Fe_2Cy_{12}$. Filter again, if necessary.

CySH.—A blood-red coloration, which is destroyed by $HgCl_2$ and not by HCl (the red colour which acetate imparts to a solution of Fe_2Cl_6 is destroyed by HCl).

H_4SiO_4.—To a separate portion add NH_4Cl or $(NH_4)_2CO_3$ a gelatinous precipitate, requiring no further confirmation, since SiO_2 is left on evaporating the filtrate from Group II.

2. HNO_3 Solution.

If present:

HCl.—On the addition of $AgNO_3$ a white curdy precipitate, very soluble in NH_4OH.

HBr.—On the addition of $AgNO_3$ a yellowish-white precipitate, less easily soluble in NH_4OH. Confirm by adding chlorine water to the original solution, and shaking up with CS_2. Bromine colours the CS_2 to a reddish-brown.

For the detection of HBr and HCl in the presence of one another, see the reactions of those acids.

HI.—On the addition of $AgNO_3$ a yellowish-white precipitate, almost

insoluble in NH_4OH. Confirm by the blue colour imparted to starch paste by the iodine liberated by chlorine water or addition of a nitrite to the acid solution.

Detection of HCl and HI in the presence of each other.—The two acids are precipitated by $AgNO_3$. The precipitate is digested with NH_4OH and filtered, AgI being insoluble in NH_4OH, dilute HNO_3 reprecipitates white AgCl from the filtrate. This is a partial separation only.

Detection of HCl, HBr and HI in the presence of each other.—Precipitate the HI as Cu_2I_2, by means of $CuSO_4$ and $FeSO_4$ or $CuSO_4$ and metallic Cu, or $CuSO_4$ and a sulphite or SO_2 solution, and filter. Boil off the SO_2 from the filtrate, and test a part of it for HBr by chlorine water and CS_2, and to the rest add HNO_3 and excess of $AgNO_3$. Wash the silver precipitate by decantation, and agitate it with water containing a little NH_4OH. Filter and add HNO_3 to the filtrate to reprecipitate the AgCl.

(i) HCy.—*Distinction between HCl, HBr, HI, and HCy.*—Test specially for HCy before proceeding to the examination of the other acids as described, by treating a small quantity of the original substance in a porcelain dish with very dilute H_2SO_4, and causing the evolved HCy to act upon a drop of yellow $(NH_4)_2S$ on filter-paper, contained in a second porcelain dish inverted over the one containing the mixture. The NH_4SCy which is formed gives a blood-red colour upon adding Fe_2Cl_6, if a "single" cyanide was present.

(ii) HSCy
(iii) H_4FeCy_6
(iv) $H_6Fe_2Cy_{12}$
} are likewise precipitated on the addition of $AgNO_3$, and are insoluble in dilute HNO_3. The second and third form salts which are insoluble in NH_4OH, whilst AgCy and $Ag_6Fe_2Cy_{12}$ are readily soluble. These acids are, however, best detected in the portion acidulated with HCl.*

3. Acetic Acid Solution.

If present:

HF.—Add $CaCl_2$, a white gelatinous precipitate. H_2SO_4 may also be precipitated by $CaCl_2$ in a strong solution; it is therefore necessary invariably to test specially for HF by etching on glass.

$H_2C_2O_4$.—A white precipitate of CaC_2O_4 is obtained, which on ignition leaves $CaCO_3$, soluble with effervescence in acetic acid. (Calcium fluoride is not affected by ignition.) On igniting the mixture the residue can be examined for CO_2 by dilute HCl and for HF by H_2SO_4 and its effect on the glass of the test tube. To the filtrate or solution if $CaCl_2$ be without effect.

H_2CrO_4.—Add to one portion lead acetate a yellow precipitate of $PbCrO_4$.

* No other cyanogen compound but a cyanide gives off HCy when treated with very dilute H_2SO_4 and it is therefore possible also to distinguish HCy in the presence of HSCy, HOCy, H_4FeCy_6, $H_6Fe_2Cy_{12}$.

H_3PO_4.—Add to another portion Fe_2Cl_6 a yellowish-white gelatinous precipitate, from a solution of a soluble phosphate or a phosphate decomposable by boiling with Na_2CO_3. Arsenic acid, if present, should be first removed by treatment with SH_2.

Phosphoric acid will, of course, have been found during the examination for bases by the molybdate.

I. NEUTRAL SOLUTION.

Tartaric acid.—On the addition of $CaCl_2$ a white precipitate which is crystalline, or becomes so, obtained by vigorously shaking or on standing. Treat the tartrate of lime, after thoroughly washing, with a strong cold solution of NaHO. After a short time the precipitate dissolves, and on heating it is re-precipitated in a gelatinous form. Characteristic reaction for tartaric acid.

Citric acid.—On the addition of $CaCl_2$ in excess, no precipitate is obtained from the neutral citrate till the solution has been boiled. The precipitate is insoluble in NaHO, but dissolves in NH_4Cl; upon boiling neutral citrate of lime separates again; now no longer soluble in NH_4Cl.

Boric acid.—Boric acid is sometimes indicated in the preliminary examination by the swelling up of some of its compounds, and the precipitation of HBO_3 in crystals from a concentrated solution of a borate, with moderately dilute H_2SO_4 or HCl. More delicate, however, is the reaction which boric acid gives with turmeric paper, and to the Bunsen flame.

Benzoic acid.—On the addition of Fe_2Cl_6 a pale yellow precipitate. Confirm by the reactions which a benzoate gives in the preliminary examination, since a precipitate of $Fe_2(HO)_6$ is frequently mistaken for ferric benzoate, owing to imperfect neutralisation.

Succinic acid.—On the addition of Fe_2Cl_6 a reddish-brown precipitate.

Separation of Benzoic and Succinic Acids.—Precipitate the two acids with Fe_2Cl_6, warm the washed precipitate with ammonia, filter, concentrate the solution, divide it into two parts and mix one part with hydrochloric acid, the other with barium chloride and alcohol. Ba succinate precipitates amorphous and almost at once, and benzoic acid forms crystals after some little time.

Formic acid.—On the addition of Fe_2Cl_6 a red coloration, and on boiling a reddish-brown precipitate, similar to that produced by acetic acid. If no substance capable of precipitating mercuric chloride be known to be present, heat with $HgCl_2$ to between 60° and 70° and observe if any reduction takes place.

Acetic acid.—On the addition of Fe_2Cl_6 in excess, the fluid acquires a deep red colour, owing to the formation of ferric acetate. If the solution is nearly neutralised and boiled, the whole of the acetate is precipitated of a reddish-brown colour.

Special tests should be applied in all cases. (See the reactions of separate acids.)

TABLE FOR THE ANALYSIS OF CYANOGEN COMPOUNDS INSOLUBLE IN ACIDS.

Method I.

N.B. 1.—All the single cyanides are decomposed on boiling with concentrated HCl into metallic chlorides and hydrocyanic acid.

Ag_4FeCy_6, $Ag_6Fe_2Cy_{12}$, and AgCy are decomposed into AgCl by boiling with aqua regia. Mercuric cyanide (soluble in water) is decomposed by SH_2.

Before using either of these Tables, it is advisable to make certain that insoluble ferro- or ferri-cyanides are really present in the substance under examination. They will have been indicated in the dry way by the odour of cyanogen emitted on heating in a tube, or in solution, when the original substance is treated with HCl, by the characteristic blue or green colour of the solution or of the insoluble residue.

To test for the presence of insoluble Double Cyanides.—Boil a portion of that part of the original substance which is insoluble in dilute HCl with caustic soda, filter; acidulate the filtrate with HCl, and test for H_4FeCy_6, $H_6Fe_2Cy_{12}$ by means of Fe_2Cl_6 and $FeSO_4$ (see reactions of acids in HCl solution).

Insoluble double cyanides are present.

Boil the portion of the original substance intended for analysis with water until the soluble portion is entirely removed.

A. Aqueous Solution.—Examine in the usual way by Tables I., II., III., IV., and V., and for acids indicated as possibly present by the preliminary examinations.

Insoluble Residue from A.—Boil with a strong solution of potassium or sodium hydrate, add a little carbonate of soda, and boil again for some time; filter and wash the residue well with hot water. The residue is now free from cyanogen unless silver cyanide was present.

Residue from Sodium Hydrate Extraction.—Dissolve in HCl and examine for bases (including phosphates perhaps) except K and Na.

The soda solution may contain other acids besides ferro- and ferri-cyanides separated from their bases by boiling with caustic soda and sodium carbonate, also those oxides soluble in alkalies, *e.g.*, SiO_2, Al_2O_3, ZnO, PbO, &c., and AgCy.

Pass SH_2 through the alkaline solution until the solution smells strongly of the gas, add a few cc. more soda, heat moderately for a short time and filter, wash precipitate well, and set it on one side.

This precipitate may contain HgS, PbS, CuS, ZnS, AgS, &c., some of which may have passed into solution in the sodium hydrate through the agency of organic matter.

The solution after removal of ZnS, AgS, and part of Group II. may still contain As, Sb, Sn, soluble in excess of soda, and HgS soluble in SNa_2. Acidify with dilute H_2SO_4, and filter. Wash well, and examine this precipitate for the metals indicated.

The sulphuric acid solution may still contain those metals which when in combination with cyanogen form compound radicles; Fe, Co, &c., and alumina. Examine it for alumina; the other metals will be detected among the acids.

Examine a part of the caustic soda extract, especially for the complex cyanogen acids.

Method II.

Heat the portion of the original substance intended for analysis in solution with pure concentrated H_2SO_4 in a porcelain basin for some time; remove the greater part of the acid by evaporation, dilute and filter. Set the acid solution aside.

Residue, boil with HCl (N.B. 1), and having dissolved out all that is soluble, add it to the first solution.

Evaporate the mixed acid solutions and examine for bases as usual.

Residue left after treating with HCl may contain Ba, Sr, Pb, &c., converted into sulphates by treatment with sulphuric acid, also silica and other substances insoluble in the first instance (N.B. 2).

Wash well, dry, and examine this as an ordinary insoluble residue.

The examination for cyanogen acids is conducted in a solution prepared by boiling some of the original substance with caustic soda and sodium carbonate, filtering and acidifying.

N.B. 1.—Sulphate of lead is decomposed by boiling with concentrated HCl.

N.B. 2.—It is advisable to test a portion of this residue in the dry way to ensure absence of metals, which might alloy with platinum.

Method III.

The double cyanogen acids may be destroyed and the bases obtained as sulphates by heating the substance with two or three times its bulk of a mixture of ammonium nitrate and sulphate. The ignition should be stopped before all the ammonium salts are volatilised, and the residue examined as usual for bases. The examination for acids is done in a solution prepared as described above.

SILICATES.

With the exception of those of potassium and sodium all silicates are insoluble in water or nearly so.

A few silicates are insoluble in concentrated HCl or H_2SO_4, but the greater number are either partially or entirely decomposed by these acids when heated with them.

Most rocks are mixtures of several silicates, of which some are often decomposable by acids; others are not. If, therefore, it is considered necessary to ascertain, as far as possible, the actual composition of the silicate under examination, it is advisable to examine separately those constituents which show a different deportment with acids. Silicates, such as kaolin and common clays, can frequently be decomposed either wholly or partly by concentrated sulphuric acid; many natural silicates yield more or less silica on treatment with hydrochloric acid, which silica may be taken to represent the soluble silica, or the decomposable silicate, leaving the greater portion of the mineral behind in an insoluble condition.

If the ultimate analysis only is required without reference to how the elements are combined, the silicate may be at once decomposed by fusion with fusion mixture.

In this case the alkalies must be tested for in a separate portion.

DECOMPOSITION OF SILICATES BY FUSION WITH FUSION MIXTURE.

The silicate is first pulverised very finely in a steel or agate mortar, then intimately mixed with four or five times its weight of pure fusion mixture, and heated in a platinum crucible as long as any CO_2 is given off. The heating may require to be completed over a powerful blowpipe.

A platinum crucible can be employed with safety only when the absence of easily reducible and fusible metals has been established by a preliminary examination of the siliceous substance in the dry way.

The silica is thus obtained in combination with the alkalies and dissolves in boiling water (TiO_2 if present in the silicate is found in the residue insoluble in water on long boiling); while the bases (CaO, MgO, Al_2O_3, Fe_2O_3, &c.) are left as insoluble oxides or carbonates, and are separated by filtration.

Residue insoluble in Water.—Dissolve in HCl and examine the solution for bases, except K and Na.

Alkaline Solution.—Examine for acids, especially silicic acid.

(N.B.—TiO_2 if present will be found partly with the SiO_2; most

of it, however, will be found in the portion insoluble in water, if the fused mass has been dissolved by long boiling.)

Detection of the Alkalies in all Silicates.

About 1 gram of the finely pulverised silicate is mixed with 1 gram of pure powdered ammonium chloride and 8 grams of pure carbonate of lime. The ingredients are thoroughly mixed in a mortar and introduced into the platinum crucible, which is gently tapped and the contents shaken down tight. The crucible is loosely covered by the lid, and heated to a bright red heat for from 40 to 60 minutes.

The crucible is now allowed to cool, and when cold the contents will be found to be more or less agglomerated in the form of a semi-fused mass. A glass rod will generally detach the mass, which is then to be heated with about 60 cc. of distilled water, when it may slake and crumble after the manner of lime. At the same time water is put into the crucible to shake out any small adhering particles, and this is added to the contents of the other vessel.

By this treatment with water the excess of lime used is obtained as a hydrate, some of the lime is combined with the silica and other ingredients of the silicate in an insoluble form; and in solution there is the excess of chloride of calcium formed during the reaction, together with the alkalies present in the silicate.

The contents of the vessel are filtered, the residue on the filter is well washed with distilled water, and the washings added to the main solution. The residue is neglected.

Solution.—Precipitate the lime with a solution of pure $(NH_4)_2CO_3$, filter and wash, evaporate the solution on the water-bath to about 40 cc., when a little more $(NH_4)_2CO_3$ and NH_4OH should be added to precipitate the small amount of calcium that escapes precipitation before. Filter through a small filter, wash, and evaporate to dryness on a water-bath, preferably in a platinum dish.

When dry, the dish is very gently heated by a Bunsen flame to drive off the ammonium chloride. Gradually increase the heat until a little below redness.

Nothing now but the pure alkaline chlorides should remain.

Test the residue in the usual way for potassium and sodium or lithium.

This process may be followed as a quantitative one to obtain the collective alkalies from a silicate.

Examples how to Record Work.

(A.) EXAMINATION OF A SIMPLE SALT.

Preliminary Dry Examination.

Substance given: white crystalline, readily soluble in water, reaction of solution alkaline.

Date & Hour.	Experiment.	Observation.	Inference.
	Gently heated some of powdered substance in bulb tube.	Gave off water, then fused; was slightly blackened; gave off CO, burning with a blue flame. Water in tube slightly acid.	Oxalate, formate, or other organic acid salt.
		Residue.—Black, alkaline to wet litmus-paper and effervesces with HCl.	Organic salts of an alkali metal.
	Heated on charcoal.	Burns partly, and sinks into charcoal, no solid residue.	
	Heated on platinum wire.	Violet flame.	Potassium.

Examination of Solution for Base.

As there is no solid residue on charcoal and no indication of a heavy metal in the residue in tube, and no sublimate, metals of Groups I., II., III., IV. can scarcely be present.

Ignited about three grams of the salt on platinum foil, dissolved in HCl, added $PtCl_4$, evaporated nearly to dryness, and added alcohol, *yellow crystalline* precipitate. Presence of K.

Preliminary Examination for Acid.

Experiment.	Observation.	Inference.
Heated with dilute HCl.	No visible result. . .	CO_2, &c., absent.
Warmed with concentrated H_2SO_4.	Gases, slightly combustible given off; taper extinguished, slight blackening.	
Passed gases into lime-water in inverted test-tube in dish and applied a light to the unabsorbed gas.	White precipitate in lime-water; gas burnt with blue flame.	CO and CO_2 probably from decomposition of oxalate or other organic acids.

Examination of Solution for Acid.

As neither HCl nor H_2SO_4 indicated presence of a mineral acid, acidulated with acetic acid and added $CaCl_2$; an immediate white precipitate which dissolved in HCl.

Presence of oxalic acid. Found; metal K; acid, $\begin{matrix} OCOH \\ OCOH \end{matrix}$.

(B.) EXAMINATION OF A MIXTURE.

Preliminary Dry Examination.

Compound given: a dirty white powder.

Experiment.	Observation.	Inference.
Gently heated in a bulb tube.	Substance first fused. Then heavy white fumes formed, which condensed in the upper part of the tube . .	Probably compounds of NH_3, Hg, As, &c.
Heated stronger.	Gave off *reddish-brown* fumes and a gas which supported combustion. The residue was yellowish whilst hot, dirty white on cooling . .	Nitrates of heavy metals. Lead, tin, or bismuth probably present.
Heated a portion of the substance, mixed with charcoal—soda-lime in tube.	Odour of NH_3, litmus blued, mirror and metallic globules *in tube.*	NH_3 *and Hg compounds.*
Heated on charcoal in the blowpipe flame.	Substance gave off heavy fumes, and was partly reduced to the metallic state. The metal malleable and marked paper; incrustation yellow .	Pb.
Heated on platinum wire.	Light-blue flame, followed by a reddish-yellow colour. Wire seemed to melt . . .	Pb, Sb, &c. Ca. Pb, &c.
Borax-bead.	Yellowish hot, but not definite.	Absence of Cu, Ni, Co, Cr, Mn, Fe, &c.

Examination in Solution for Bases.

Substance dissolved partly in water, partly in HCl with evolution of CO_2. On mixing the two solutions, acicular crystals fell out; probably lead as chloride. Filtered off; boiled crystals with water and added K_2CrO_4. Yellow Pp. *Passed a current of SH_2 through filtrate from lead chloride crystals.*

<table>
<tr><td rowspan="4">A black pp. Group II. present.</td><td colspan="4">Evaporated filtrate till free from SH_2, added a few drops of HNO_3 and evaporated to near dryness, added 1 cc. HCl and then ammonium chloride and ammonia.</td></tr>
<tr><td rowspan="3">No pp. Absence of Fe, Cr, and Al.</td><td colspan="3">Solution passed SH_2.</td></tr>
<tr><td rowspan="2">No pp. Absence of Zn, Mn, Ni, and Co.</td><td colspan="2">To the same solution added $(NH_4)_2CO_3$.</td></tr>
<tr><td>A white pp. Group IV. present.</td><td>Solution.—Evaporated to dryness and ignited. No residue. Absence of Mg, K, Na.</td></tr>
</table>

Examination of Precipitate produced in Group II.

Washed precipitate till free from HCl, and boiled with $(NH_4)_2S$. Filtered.

<table>
<tr><td colspan="3">Residue.—Boiled with HNO_3 only partially dissolved, Mixed with OH_2, and added dilute H_2SO_4, warmed and filtered.</td><td rowspan="3">Solution. Acidulated with dilute HCl. No yellow precipitate. Absence of As, Sb, and Sn.</td></tr>
<tr><td colspan="2">Residue.—Boiled in ammonium acetate and filtered.</td><td rowspan="2">Solution. — SH_2 added to a portion of solution gave no precipitate. Absence of Bi, Cu, Cd. *Neglected remainder.*</td></tr>
<tr><td>Residue. — Dried, ignited in a bulb tube, with dry Na_2CO_3. Metallic mirror and globules. Presence of Hg.</td><td>Solution.—Added K_2CrO_4. yellow precipitate. Presence of *Pb*.</td></tr>
</table>

Examination of Precipitate produced in Group IV.

Dissolved precipitate in acetic acid and added K_2CrO_4.

No pp. Absence of Ba.	Solution.—Added ammonium sulphate, and allowed to stand for ten minutes.	
	No pp. Absence of Sr.	Solution.—Added ammonium oxalate. A white precipitate, Ca present.

Preliminary Examination for Acids.

Experiment.	Observation.	Inference.
Treated with dilute HCl.	Effervescence. The gas precipitated lime-water.	CO_2.
Treated with concentrated H_2SO_4.	Cl and nitrous fumes; bleaches litmus-paper; test-tube not etched .	HCl and HNO_3. Abs HF.
Confirm HNO_3 by means of H_2SO_4 and $FeSO_4$.	A brown ring formed . .	HNO_3.

Examination of Solution for Acids.

Dissolved in dilute HCl and filtered.	Dissolved in dilute HNO_3 and filtered.
Added $BaCl_2$, no precipitate, H_2SO_4 absent.	Added $AgNO_3$, white curdy pp., soluble in AmHO. Presence of HCl.
This was hardly likely as Pb was present in a soluble form.	Warmed original substance with MnO_2 and H_2SO_4 yellow gas = Cl.

Ammonium molybdate, no results: abs P_2O_5. Moistened with strong H_2SO and alcohol added and inflamed, no yellow-green flame: abs B_2O_3.

Found—Bases: Hg, Pb, Ca, NH_3.
Acids: CO_2, HNO_3, HCl.

APPENDIX I.

QUANTITATIVE EXERCISES.

The main difference between quantitative and qualitative work consists in the fact that in the former weighed quantities of material are operated upon, and the product, or products, are also weighed. Otherwise it does not require much more apparatus than ordinary qualitative work.

A balance of some degree of sensibility is, of course, a necessity. A very simple one will, however, do for many purposes at first. Besides this, a few porcelain crucibles, and perhaps a platinum crucible, are required. A few moderate-sized beaker-glasses, and a copper or iron drying-oven, with thermometer, are useful.

Instruction in weighing is always better obtained practically than can possibly be given by written description, but with a little attention to one or two points satisfactory results can be obtained.

Gramme weights are most usually supplied to a balance, and the balances, as a rule, are sensitive to ·001 of a gramme or less. For the purposes of these exercises one responding to ·01 of a gramme will be enough.

The weights, supplied in boxes, are generally arranged from 50 grms. thus :—50–20–10–10–5–2–1–1–1, and ·5–·2–·1–·1–·05–·02–·01–·01, with some smaller, which are seldom used. If the balance-case be wide enough, which they seldom are, being made by rule of thumb for sale, the weights are best arranged on a piece of tile or paper inside the case ; they are then more easily accessible.

The theory of the balance cannot be entered into here.

When commencing to weigh, place first the substance on one pan ; then commence by putting on the opposite pan the largest weight of the set. Slowly turn the handle, which generally relieves the balance-beam from its supports, and watch the direction of motion of the indicating needle on the scale in front. When it points in the direction of the pan on which are the weights, it indicates that more are required. Then add the next greater weight, bringing the balance to rest between each addition by turning up the beam supports. This must never be omitted. Never jump or guess at the weight, but always proceed by putting on in order from the greatest. As the correct weight is approached the balance will begin to swing slower. Do not wait until the beam comes to rest, but proceed by the addition or taking away of weights until the needle swings nearly an even distance on each side of the centre mark of

the scale. Let it swing three or four times. It will probably on first turning the beam loose swing to 6 on one side, and swing past the centre to 8 or 10. If the beam is provided with a rider, now is the time to use it. Say the needle swings to 6 left, and recovers to 8 or 10 right, then more weight is wanted on the right side of beam. Place the rider on, this time beginning at the middle of beam, or the mark 5, and again swinging, move the rider to less or

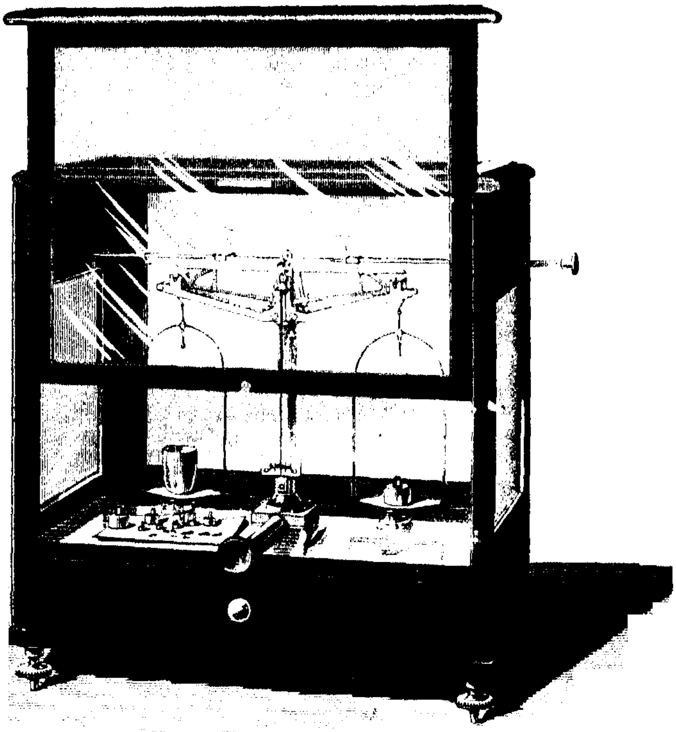

FIG. 25.

more than 5, as the needle indicates. When it swings nearly evenly, turn up the beam to rest, and then carefully again liberate. It should be set swinging five or six degrees, and allowed to swing several times before arresting. If equilibrium has been obtained the swing will diminish regularly on each side of the centre. Bring to rest, and read off the values of the weights from the empty spaces, either in the weight-box, or on the paper referred to as holding them in the balance-case. Pick the weights from the pan, and replace them in order, seeing at the same time that they tally with the weight recorded.

The order of the experiments here indicated may no doubt be altered with advantage under certain circumstances. They need not be followed strictly in this order, although it has been found to work well.

RELATIVE COMBINING WEIGHTS.

Atomic and combining weights of the elements are in some cases identical values, as, for instance, with chlorine and hydrogen. With oxygen and hydrogen the atomic weights are as 16 to 1, and the combining, or equivalent weights, as 8 to 1. Few metallic substances combine directly with hydrogen, whilst many combine most readily with oxygen or sulphur, or chlorine, or iodine, and these in turn combine easily with hydrogen, so that indirectly the combining weights may be obtained as compared to H as unity.*

As easy practical examples, the combinations of copper, silver, lead, and iron with oxygen or sulphur or iodine may be taken first.*

A. **SILVER AND SULPHUR.**—Carefully clean and weigh a small porcelain crucible with its lid. Place in the crucible about a square inch of silver, thin sheet or foil, or better, as granulated metal. The quantity need not exceed 1·5 grm. and may be as little as ·2 grm. Weigh the crucible with silver. The difference in the two weights gives, of course, the weight of silver taken. Place the crucible on a triangle of tobacco-pipe stem, supported on a tripod or other arrangement, so that it can be heated to redness by a Bunsen flame. When nearly red hot lift the lid and drop in a piece of roll sulphur; replace the lid. The sulphur need not be weighed, but should be somewhat heavier than the silver taken. Continue heating strongly, until all fumes of sulphur cease to come off. Repeat the dose of sulphur and heating, then allow to cool, and weigh. The lid must be kept on the whole time, and until quite cold. The product should have fused to a black mass. It will be found to have increased in weight by the sulphur taken up. The increase should be in the proportion of 108 becoming 124, or 108 parts silver combine with 16 of sulphur to form silver-sulphide, from which the formula is Ag_2S.

ACTUAL EXAMPLE.

Weight of porcelain crucible . .	15·244	=	Silver
,, ,, ,, and silver .	15·567		·323
After heating with sulphur . .	15·608	=	Silver sulphide
Less crucible	15·244		·364
Sulphur taken up . . .	= 364 – 323	=	·041

This is = 12·7 per cent. of contained sulphur. The formula Ag_2S demands 12·9 per cent. sulphur. With this amount of sulphur uniting with silver the formula may be derived, thus:

* Refer to the Table of Atomic Weights in performing the calculations required for these experiments.

$$S\% \quad \frac{12 \cdot 7}{32} = \cdot 4 \text{ (nearly)} = 1$$

$$Ag\% \quad \frac{87 \cdot 3}{108} = \cdot 808 \;\; ,, \quad = 2$$

32 and 108 are the atomic weights of sulphur and silver respectively, and dividing the percentage found by these values, gives the relative number of atoms of each in the compound. These are generally reduced to the smallest expression, unless some proof of the constitution of a compound is to be had.

The above values come nearer on taking the more revised atomic weights given in Table on page 9.

B. **COPPER AND SULPHUR.**—The corresponding experiment with copper is somewhat less easy. It is carried out in precisely the same way.

Weigh out in the porcelain crucible, or even in a test-tube of good glass, one to two grms. of copper, either as fine wire or thinnish sheet, heat up to redness with the lid on, and then add sulphur and heat more strongly, still with the lid on, until the excess of sulphur has evaporated. Repeat the heating with sulphur and finally cool by allowing the unignited coal-gas to escape and flow around the crucible. *Air must not come in contact with the copper sulphide until it is cool.* The product should be a blue crystalline substance of the composition Cu_2S in which 63×2 parts of copper are united with 32 of sulphur. Unless the heating be somewhat severe too much sulphur will be found, as a sulphide of the composition CuS is first formed and then decomposed by a high temperature.

LEAD AND SULPHUR.—Actual example. Crucible was weighed, lead introduced and weighed again; placed on tripod and heated, and sulphur added, the heating continued over the blowpipe flame for 30′. Cooled and weighed again.

I.	Crucible		23·451
II.	,, ...	+ lead	24·804
		lead =	1·353
III.	Final weight after heating with S	=	25·022
IV.	Less crucible	=	23·451
		Lead sulphide =	1·571

This lead sulphide contains ∴ 13·87 per cent. sulphur. The formula PbS requires 13·38 per cent. sulphur and 86·62 lead.

Taking the amounts found, $\frac{13 \cdot 87}{32} = \cdot 4335$ S and $\frac{86 \cdot 13}{207} = \cdot 4082$ Pb, or nearly atom to atom.

C. **COPPER AND OXYGEN.**—If a supply of oxygen be to hand the copper sulphide in the experiment B can be converted into oxide by a direct action. For this purpose heat the crucible containing the Cu_2S over a good flame with the lid off, and blow a gentle stream of oxygen gas from the cylinder on to the substance. It will glow brightly. Sulphur dioxide will be formed and escape as gas and CuO remain in the crucible. The heating should be continued for some time, 15′ at least, and finished over the blowpipe flame, if possible, but with the stream of oxygen gas the whole time.

The operation is most satisfactory, however, if carried out in a muffle, as there is some danger of loss by blowing oxygen into the crucible unless the current of gas is very gentle.

D. **TIN** may be treated with sulphur in a similar manner to copper (B).

The product is SnS. It is somewhat more difficult to get exact figures, however, unless a good blowpipe flame is available. The same applies to lead.

If a "muffle" be available these sulphides may be converted into oxides in a short time, as with Cu_2S.

E. **SILVER, OR LEAD, AND IODINE.**—Weigh out in a porcelain crucible 1·0 to 2 grms. silver, as thin sheet or foil, heat up nearly to redness and drop in crystals of iodine (the operation should be done under a draught). The silver should glow brightly when uniting with the iodine and melt into a colourless liquid; add iodine once or twice again to make sure that all the silver is combined; cool and weigh.

In this case air has little or no effect either when the iodide is hot or cold.

ACTUAL EXAMPLE.

Crucible	22·1442
Crucible + Ag	22·5280
∴ Ag =	·3838
After heating and adding iodine until product melted into nearly colourless mass	22·9775
Less crucible	22·1442
	= ·8333 AgI.
Less silver	·3838
= Iodine	·4495 taken up.

The iodide formed contains ∴ 46·06 per cent. iodine.
Calculated for AgI = 46·0

Or $\frac{\text{Amount of Ag}}{\text{Atomic wt. of Ag}}\ \frac{·3838}{108} = ·355$

$\frac{\text{Amount of I.}}{\text{Atomic wt. of I.}}\ \frac{·4495}{127} = ·354$

Or atom to atom as nearly as possible.

With lead it is best to add the iodine to the cold metal in the crucible after weighing, and then heat them up together. It will require also several repetitions of the iodine treatment. 103·5 parts of lead take up 127 iodine. With a very slight modification of apparatus chlorine may be employed instead of iodine, and the results with silver are even sharper than when iodine is used. It requires no more apparatus than a good chlorine generator. The metal can be heated in a crucible and the Cl gas led in with a small glass tube, taking care not to touch the red hot crucible with the tube.

A bent tube, as in Fig. 26, allows of several chlorides being

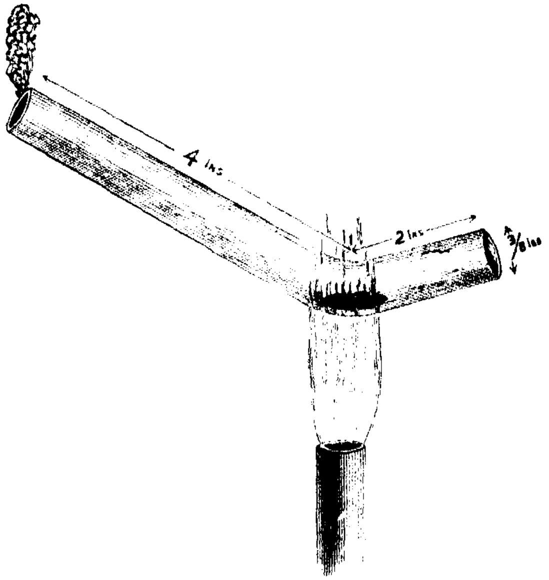

FIG. 26.

made quantitatively, the tube being weighed first empty and dry, then with the metal and finally after chlorination.*

F. If compressed oxygen be obtainable, the combining weights of several metals as regards that element may be determined by direct combination.

LEAD AND OXYGEN.—Clean and dry a piece of hard glass tube of about 6 inches in length, and then weigh it. Insert

* This form of tube serves to heat up a weighed amount of some metallic sulphide, as PbS or Ag_2S, which is then heated in the slow current of air caused in the tube by natural draught. In this case a certain amount of sulphate is produced. The experiment should be done with silver sulphide, which forms almost the theoretical amount of sulphate, and with lead sulphide which scarcely forms half the theoretical.

a small piece of pure lead about 2·0 grms. or less and weigh again. See that the lead is about one-third of the length of the tube from one end. The tube need not be bent for infusible metals as copper. Hold the tube in a clamp on the retort-stand, and heat carefully until fully melted. Now direct a gentle current of oxygen by a tube attached to the oxygen cylinder into the tube. At the same time heat up as strongly as possible. The lead will burn, and form PbO, which fuses and melts a depression in the wall of the tube. A little lead generally remains unacted upon. Weigh the tube again, break up and extract the small globule of lead, which weigh separately, and deduct its weight from that of the lead originally taken. With ordinary care the results come very close to those theoretically required for PbO—that is, 207 lead to 16 oxygen.

EXAMPLES OF DISPLACEMENT, OR EXPULSION OF ONE ELEMENT, OR GROUP OF ELEMENTS, BY ANOTHER, OR BY HEATING.

This is a very commonly occurring method of chemical action. One of these has been already indicated—the replacement of sulphur by oxygen.

Many crystalline salts contain water. This water is in many cases expelled by heating the salt to, or a little above, the boiling point of water. Sometimes a red heat is necessary to expel the whole of the water. This high temperature can, however, only be applied in some cases where no further decomposition takes place excepting the crystal water. As an example of this, sodium phosphate, or borax ($B_4O_7Na_2 + 12H_2O$), or sodium sulphate may be taken. Weigh about ·5 to 2·0 grms. of the salt in a small dish or crucible, heat for some time in a hot-air oven, and finally over the blow-pipe to complete fusion. Care must be taken during the heating that the substance does not spirt. The first part of the drying should always be done in the hot-water or steam oven. The dish and substance is then placed in a desiccator to cool before weighing. The heating must be repeated until the weight finally becomes constant.

It will be found an advantage if the student prepares for himself a number of salts with water of crystallisation, or constitution as it is termed in some cases, and determines this water by heating up to different temperatures in an air-bath.

ACTUAL EXAMPLE.

Copper sulphate,* crystallised.	
Crucible	15·4775
Crucible + salt	18·8679
Salt taken	3·3904
Heated for one hour at 100° C . .	17·8800
=	·9879 loss.
=	29·16 % loss at 100°.

* The copper sulphate taken for this example should be purified by several crystallisations. See crystallisation of lead nitrate, and copper sulphate under those metals, *ante*.

Heated again in air bath to a little above 200°	= 17·6397	
	17·8800	
Loss at 200°	= ·2403	
	= 7·37	per cent.
Total loss	= 36·53	
Calculated for $CuSO_4$, $5H_2O$.		
Total water	= 36·13	per cent.

Nitrates, chlorates, carbonates, and other salts, when heated to a moderately high temperature alone undergo decomposition of a more or less complex nature. In some cases it is, however, within *certain ranges of temperature, quite sharp and definite*, admitting of employment as an exercise.

POTASSIUM CHLORATE when heated loses all its oxygen, becoming KCl.

As a quantitative experiment this can be performed in a weighed test tube if only a small quantity of the salt be taken, say ·2 to ·5 gram. *Weigh the clean dry test-tube, introduce the dry salt* in fine powder, weigh again. Then heat very gently until the whole of the salt is melted; keep melted for some time, very gradually increasing the temperature so that the oxygen does not come off too rapidly. The tube is best inclined, or a watch-glass placed with convex side down, on the tube. With a little care there will be *no* loss from spirting. Weigh immediately after cooling in a desiccator, as the KCl absorbs moisture somewhat rapidly.

CALCIUM CARBONATE ($CaCO_3$).—Weigh out in a platinum or porcelain crucible about ·5 to 1·0 grm. pure Iceland or calc spar. Heat over the blowpipe as strongly as possible for 30′. *Cool, and weigh again. Repeat the heating and weighing until a constant weight is obtained.*

The loss in weight should be close upon 44 per cent.

$$\text{For } \underset{100}{CaCO_3} = \underset{56}{CaO} + \underset{44.}{CO_2}.$$

A little pure cane sugar, which need not be weighed, placed in the crucible, assists in liberation of the CO_2. The crucible must, however, be left partly open, to burn off any carbon from the sugar.

Alkaline carbonates heated alone do not give off the whole of the CO_2, but when heated with acids, or acid salts, the CO_2 is expelled.

SODIUM OR POTASSIUM CARBONATE; and an acid salt.—Weigh about ·5 grm. of dried sodium carbonate into a moderate-sized crucible. Cover it with at least five times as much potassium dichromate that has been melted, and then pounded up finely. Weigh again. The difference gives amount of sodium carbonate and potassium dichromate. Now heat gently over a Bunsen burner until the whole is in quiet fusion. Continue the heating for

fully 20 minutes; cool and weigh. Heat again for a few minutes *carefully* over the blowpipe. The weight should be constant.

The reaction taking place, if the temperature has not been too high, is—

$$K_2Cr_2O_7 + Na_2CO_3 = CO_2 + \begin{cases} Na_2CrO_4 \\ K_2CrO_4 \end{cases}.$$

Silica, SiO_2, may be used for this experiment instead of dichromate if it can be obtained as precipitated silica.

The process is then similar—viz., weigh the crucible and SiO_2 taking a considerable excess of SiO_2. Then add and weigh about ·5 grm. of the carbonate; mix carefully by means of a platinum wire in the crucible, place on the lid and heat, gently at first, finally over the blowpipe flame as high as possible for 20′; the loss of weight should be CO_2 only, according to the equation:

$$K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2.$$

If a muffle heated by gas is to be had it is far easier and better for some of these exercises than heating with the blow-pipe flame. Nitrates when heated alone are either decomposed into oxides of nitrogen and a metallic oxide or in some cases free nitrogen and oxygen are given off.

When heated with sulphuric acid sulphates are formed and with silica silicates.

The alkaline nitrates are easiest to work with as examples with silica. Weigh out in a porcelain or platinum crucible about 5 grms. of fine sand (as with the carbonates), then mix with this, by means of a wire, about ·5 grm. of potassium nitrate, weigh and then heat in the covered crucible very carefully to redness. Keep red-hot for 15′ or 20′, and then heat a little stronger over the blow-pipe for a few minutes only. The loss should be the N and O only according to the equation:

$$4(KNO_3) + 2SiO_2 = 2K_2SiO_3 + 2N_2 + 5O_2.$$

ACTUAL EXAMPLE.

Potassium nitrate and silica:

Crucible and Sand, SiO_2	31·4362
„ + KNO_3	32·3534
Nitrate taken	0·9172
Weight after heating	31·8615
Loss	·4919

Percentage loss = 53·52 = all the nitrogen and five-sixths of the oxygen.

For the equation above the loss should be 53·46 per cent.

Nitrates, carbonates, haloid salts, &c., are all decomposed easily by strong hot sulphuric acid, and as sulphates are very stable bodies

against a high temperature, as a rule, many examples of displacement may be performed. They require, however, somewhat more care with sulphuric acid than with SiO_2 and similar non-volatile acids, as B_2O_3.

CHLORINE in common salt, **IODINE** in potassium iodide, or N_2O_5 in nitre, can all be expelled by heating with strong H_2SO_4 in slight excess. Similarly with a large number of salts of other metals besides these mentioned.—

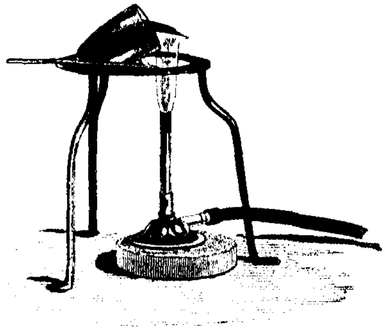

FIG. 27.

A platinum crucible is most convenient for this, but with care it may be performed equally well in an ordinary porcelain one. Weigh a crucible, place in it a small quantity of the salt, weigh again; if the quantity taken is more than 1 grm. throw some out, if under ·5 a little more may be taken. After one or two trials the amount taken will approximate to 1 grm.; arrange the crucible on a triangle that it forms almost a right angle with the perpendicular (see Fig. 27), and wedge the lid edgewise in the opening. Drop gently not more than ten drops of concentrated sulphuric acid into the crucible, wait until the effervesence has almost ceased, then place a very small flame under the protruding part of lid, so that a draught of heated gases flows over the contents of the crucible. The evaporation of the excess of sulphuric and of the volatile acid liberated takes place gradually and without spirting. When the contents of crucible appear quite dry turn up a larger flame, and finally heat strongly to redness. It is generally necessary and always advisable to add an additional quantity of the H_2SO_4, and treat as before, in order to be sure that all is converted into the sulphate.

The reaction with common salt is—

$$\underset{117}{2NaCl} + \underset{98}{H_2SO_4} = \underset{142}{Na_2SO_4} + \underset{73.}{2HCl.}$$

The others are similar.

ACTUAL EXAMPLE.

Potassium in potassium iodide, KI, by heating with H_2SO_4.

Crucible		79·8000
Crucible + KI		80·7864
KI taken		·9864
After heating with H_2SO_4 . . .		=80·3184
	Less crucible	79·8000
K_2SO_4		= ·5184

Now the molecular weight of $K_2SO_4 = 174$, and contains $K_2 = 78$. Therefore ·5184 of the salt will contain ·2323 K.

$$\frac{\cdot 2323 \times 100}{\cdot 9864} = 23\cdot 55\ \%$$ of K contained in the potassium iodide.

The formula KI requires 23·49.

In case the salt contains water of crystallisation it is better sometimes to drive this off before treating with H_2SO_4, but in most cases it does not interfere at all.

All sulphates will not stand so high a temperature as potassium or sodium sulphates, but very few are decomposed at the temperature at which sulphuric acid is completely volatilised.

PRECIPITATIONS FROM SOLUTION.—When one substance is precipitated from a solution by another, several additional operations are necessary before it can be weighed. One of the simplest examples is the precipitation of a metal, as oxide, or hydrate, or carbonate, and final conversion of this by heating into pure or anhydrous oxide of definite composition. Oxides are generally (see *ante*) bodies capable of withstanding a high temperature without change, and the advantages of this are that they may be obtained absolutely free from moisture, and that any volatile matters, which may by accident be present, are driven off during the heating. Almost any metallic salt will do for this purpose.

LEAD.—Almost any soluble salt of lead will do. The nitrate has some advantages over others. Twenty or 30 grms. of the salt should be dissolved in a small quantity of boiling water to which one drop of HNO_3 has been added. The solution is then to be cooled rapidly and stirred vigorously all the time. Small crystals will form. The water is drained away and the crystals placed between several thicknesses of good filter paper and *very gently* pressed. The papers are to be renewed as long as any moisture is evidently taken up. The crystals may then be dried in a steam oven, and finely powdered before using. If commercial pure lead nitrate be used once crystallising will be sufficient. If not of known origin the crystallising must be repeated several times until it is pure. (See Qualitative Tests.)

Weigh from a small tube or bottle a gramme or two, not more, of the salt. This is best done by having a little tube—a small test-tube will do with clean good-fitting cork—in which 5 to 10 grms. of the dried salt are contained. Weigh this tube with its contents. Take from the balance, remove the cork with the left hand and shake a small quantity of the salt carefully into a beaker glass. See that the quantity shaken out *does enter* the beaker. Hold the tube and cork over the open beaker whilst inserting the latter again. Weigh; the difference gives the amount taken. It should not be much more or less than 1 grm. To the salt in the beaker add one drop of nitric acid and then warm water—about 50 cc. Heat to boiling and then add slight excess of ammonium carbonate.

Excess means here, as usual, that a few drops added to the filtrate or the clear supernatant fluid produce no further effect. Keep warm, but not exactly boiling, for a few minutes, during which a filter paper (either plain or folded) is got ready—viz., placed in the funnel and wetted with hot water.

The folded or plaited filter papers may be employed for this work, as with care they filter more rapidly than the ordinary method of folding and with equal certainty of securing the whole of the precipitate on the paper.

The precipitate of lead carbonate will settle somewhat rapidly; pour off the liquid above the precipitate into the filter. To do this properly and safely, because ALL must go through, requires that the liquid should be poured from the beaker down a glass rod which should be held in the left hand with one end over and well towards but not touching the centre of the paper funnel or cone, and inclined at an angle: see Fig. 29, p. 264.

Every visible particle of the precipitate must be detached from the beaker and washed by a fine jet of water, from the wash-bottle, into the filter. The precipitate must then be washed by pouring hot water six or seven times over the precipitate and allowing to drain away between each addition. It is scarcely necessary to say that the filtrates must in all cases be *absolutely crystal clear* and all the *precipitate be retained by the paper.*

The test for complete washing is when a few drops of the wash-water give no appreciable residue when evaporated on a piece of glass, or porcelain dish.

The precipitate may now be dried by placing the glass funnel and filter in a drying oven, or in a dry clean place if time be no object.

The drying will be much facilitated if it be finally washed twice with warm methylated spirit. If the washing has been complete, the precipitate will detach almost completely from the paper when dried. Weigh a *porcelain* crucible during the drying of the precipitate. Spread a piece of clean writing-paper; on this place the weighed crucible; detach, by gently rubbing the paper together, the precipitate from the paper, dropping it into the crucible. Sweep any particles falling on the writing-paper into the crucible with a small dry camel's-hair brush, or a quill feather. This needs care, and nothing else should be thought about whilst doing this, as *all* the particles from the paper must come into the crucible.

The paper, from which nearly all the precipitate has been removed, must now be burnt in such a manner that all the ash, and any adhering precipitate falls also into the crucible. Have the paper folded so as to form a semicircle, and double of course; then fold up into a strip about a centimetre, or $\frac{1}{2}$ inch, wide; now start at one end, and roll up tightly into a coil, and fold a piece of platinum wire several times around.

Hold over the crucible, or better, invert the lid over the crucible, and hold the paper over this, and start burning by bringing a Bunsen flame to it as it is held. The paper will burn first with flame, and then smoulder until all the black carbon is consumed, and a greyish ash

remains, of the same shape, but much smaller than the original roll of paper. (See Fig. 28.) At this stage it should be dropped into the crucible itself. For ordinary accurate analyses, the amount of ash given by any sample of filtering paper must be ascertained. In the example it was neglected, and the effect is visible in the bad result.

The crucible, now containing the precipitate and what adhered to the paper, and the paper ash, is placed on the pipe-clay triangle and heated with the Bunsen flame to redness. It may even be heated for

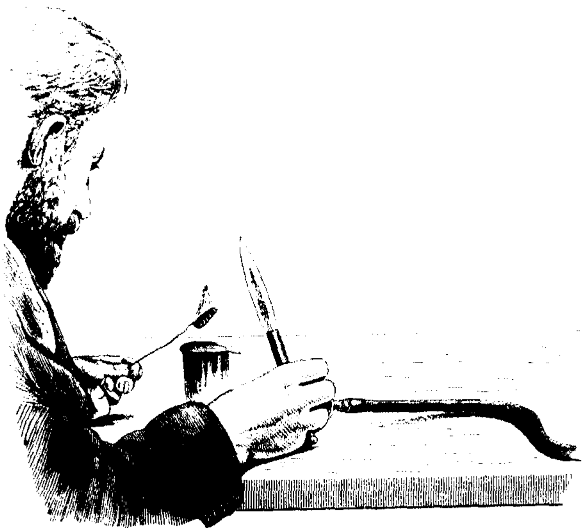

FIG. 28.

a few minutes over the blowpipe, but this is not absolutely necessary, or in the case of lead oxide advisable. Allow to cool, and weigh. It consists of lead oxide PbO.

For this exercise it is, perhaps, better to commence with pure metallic lead instead of a lead salt, and the same remark applies, of course, to some other metals besides lead. Actual example:

Assay lead and watch glass = 32·560,
Glass alone . = 31·320; lead taken, 1·240,

dissolved in hot dilute nitric acid, precipitated with ammonium carbonate, with a little ammonia, as above detailed.

Porcelain crucible . . 21·630,
Crucible and precipitate, 22·968; gives 1·338 as lead oxide.

This contains, of course, 0·098 of oxygen, so the percentage is 7·32, whilst for PbO the calculated is 7·175 oxygen.

The formula may be derived as in a previous example:

$$\text{Oxygen} = \frac{7{\cdot}32}{16} = {\cdot}457 \text{ or nearly } 1 : 1 \qquad \text{Lead} = \frac{92{\cdot}68}{207} = {\cdot}447.$$

Lead is most generally precipitated as sulphate when any other metals are present which form soluble sulphates.

Weigh from ·3 to not much more than ·6 grm. lead nitrate, or a corresponding amount of metal, dissolve in as small a quantity of hot water as possible (20 to 25 cc.). Keep warm, and add normal H_2SO_4 in slight excess. ($PbSO_4$ dissolves in very strong and in very dilute H_2SO_4, but is almost insoluble in acid of normal strength.) Then add about the same volume of alcohol. Allow to stand for some hours in a warm place, covered of course, and then pour the *clear liquid* through the filter, afterwards washing the $PbSO_4$ on to the paper with alcohol from a small wash-bottle and fine jet. The precipitate must be washed with alcohol until no acid reaction is given by the filtrate. The funnel and precipitate is placed in drying oven. Weigh a porcelain crucible; detach the dry sulphate from the paper into crucible, roll up and burn the paper thoroughly in the wire, drop the ash into the crucible, and ignite gently either over the flame or for a short time in the muffle. Cool and weigh, and then moisten with one drop of H_2SO_4 (strong), and replace in muffle. Cool and weigh again.

303 parts $PbSO_4$ contain 207 of lead.

Ash in Filter Papers.

The mineral matters in ash of filter papers is an almost constant quantity, and is generally ascertained once for all when commencing to use filter paper for quantitative purposes.

The best plan is to take several—half a dozen—filter papers, place them in a weighed crucible, either porcelain or platinum; put on the lid, and heat up until combustible gases escape. When the gases cease to escape and burn, but not before, take off the lid, and allow to smoulder away with the flame under until every visible particle of charcoal has disappeared. Close, cool, and weigh. Divide the weight found by the number of filters taken, which gives the weight (nearly) of one filter. This weight is deducted from that of any precipitate which has been burnt with a filter paper.

Example: Platinum crucible and five filter papers:

Crucible . . .	20·1635
Crucible and ash . .	20·1672
	·0037/5

gives ·0007 as the ash in a No. ⊙ Swedish paper. This is a small paper. The ash of the usual size to fill a 3-inch diameter funnel weighs about ·0046.

Had this amount, ·0046, been deducted from the weight of lead oxide, above, the result would be better.

In some cases, as, for instance, copper, nickel, cobalt, and zinc,

ammonia salts, or ammonium hydrate, cannot be employed as precipitants. They form soluble compounds with the metals (see these metals, *ante*). It is even necessary in the cases mentioned to remove all ammonia salts, and precipitate with sodium or potassium hydrate or carbonate. The carbonates are more generally applicable than the hydrates; zinc and aluminic hydrates dissolving, for instance, in sodic or potassic hydrates.

COPPER.—As an example of a hydrate precipitation copper sulphate may be taken.*

(Actual example, part of complete analysis; see water in same.)

Weighing bottle + copper sulphate	=	30·0318
" " − " "	=	28·6708
Amount of salt taken	=	1·3610

Dissolved in hot water in beaker (150 cc.), heated nearly to boiling and added, in very slight excess and gradually, potassium hydrate solution. (The KHO is added in ccs. at a time and the precipitate allowed to settle before adding another cc. It must be kept nearly at 100° during the precipitation and filtration.) Boiled for 10', allowed black precipitate to settle and filtered through folded filter paper. Washed until wash-water no longer gave an alkaline reaction to red litmus paper.† Dried precipitate, in funnel, in oven. Detached from paper; burnt paper and heated crucible, with precipitate, and ash in the muffle for 30'.

Porcelain crucible + CuO and ash	=	15·9157
" "	=	15·4803
ash	=	·0045
CuO	=	·4309

$$\mathrm{CuO} : \mathrm{Cu} :: \mathrm{CuO} : \mathrm{Cu}$$
$$79 : 63 :: \cdot 4309 : \cdot 2715$$

$$\frac{\cdot 2715 \times 100}{1\cdot 3610} = 25\cdot 26\ \%\ \mathrm{Cu}.$$

The calculated amount in $CuSO_4\,5H_2O$ = 25·33

ZINC is, when possible, precipitated from solutions not containing ammonia, by sodium carbonate as a basic zinc carbonate, which

* As in the case of the lead nitrate, it is no use taking a salt for exercise the purity of which is doubtful. Copper sulphate is easily purified by recrystallisation, after the same manner as the lead nitrate. As traces of iron are not so easy to get rid of, the process of solution and crystallising should be repeated at least three times, commencing with 40 or 50 grams of the pure commercial salt. When pressing between filter papers *do not rub.* The crystals must be obtained dry by this means only. They are liable to lose some crystal water on exposure in a warm place, and must *not* be placed in a desiccator.

† *Too* much washing can scarcely be given in any case. Small quantities of hot water several times repeated is more effective than one large dose. There is no object, however, in continuing the washing after the precipitant has been *completely removed.*

is subsequently converted into oxide ZnO, by ignition either in a muffle (best) or over a blow-pipe.

Zinc sulphate, or pure metallic zinc, may be taken as an exercise. The sulphate must be carefully crystallised from hot water and dried between paper, as it contains water of crystallisation. Commercial zinc is so impure as to be misleading for an exercise.

Zinc has frequently to be *separated* from other metals which would be precipitated by an alkaline carbonate. In these cases the zinc can be frequently thrown down as sulphide by an alkaline sulphide, and this sulphide, after washing, dissolved in HNO_3 or HCl + $KClO_3$, and then converted into oxide as above. In other cases ammonia will separate zinc from other metals, Fe, Al, Cr, in the presence of ammonia salts, moderately completely. The filtrates containing the zinc and ammonia have then to be evaporated and ignited to destroy all the ammonia salts.

Take about 1 grm. of zinc sulphate, dissolve in 250 cc. hot water, add Na_2CO_3 in slight excess, boil for some minutes until on removing the lamp the precipitate settles down moderately quickly, filter and wash well until the washings are neutral to litmus. A final washing with alcohol facilitates drying—place in oven to dry and treat as with the CuO.

In some cases where a metallic oxide is not reduced by the carbon of the filter paper, the precipitate may be placed *wet* in the weighed crucible, either porcelain or platinum, and this introduced at once into the hot muffle or heated over a good blowpipe flame. The moisture then assumes the spheroidal state, and evaporates *without spirting*. This treatment saves much time and several mechanical operations.

After ignition the zinc is left as ZnO from the basic carbonate; the sulphide also after long ignition in air becomes ZnO. The sulphate requires heating *very* strongly over the blowpipe before complete conversion into the oxide takes place.

Nickel, cobalt, and manganese salts may be treated almost exactly like the zinc salt. Suitable salts to prepare are the sulphates, as $NiSO_4.K_2SO_4$ which crystallises well. $CoSO_4$ and $MnSO_4$ do not crystallise quite so well.

They may be precipitated as carbonates by Na_2CO_3 and ignited to oxides. In the case of Ni and Co ammonium salts must be absent. With manganese it has no effect. Ammonium carbonate can be used to precipitate Mn with advantage over alkaline carbonates which are difficult to wash away from the Mn precipitate. After ignition the manganese is left as Mn_3O_4, whilst nickel and cobalt are NiO and CoO respectively.

Aluminium and chromium are best precipitated by ammonium hydrate. Alkaline hydrates and carbonates should, if possible, be absent from the solutions, as if present in large quantity they prevent the precipitation owing to the formation of soluble alkaline compounds, and when in small quantity, some of the alkali is carried down by the $Al_2(HO)_6$ or $Cr_2(HO)_6$ and is almost impossible to wash away.

ALUMINIUM.—The alums, potassium, or ammonium aluminium sulphates are the best salts to exercise on. They

should be recrystallised from hot water, as with previous examples, and also dried only between filter papers, as they contain much crystal water.

As aluminium is very light, about 2 grms. of the salt should be taken, the solution heated to boiling and ammonium hydrate added in excess, the boiling continued a few minutes and the filtration conducted as hot as possible. Wash with hot water until wash-water is almost neutral, finally with alcohol. Introduce paper and precipitate, wet, into a platinum crucible and ignite direct either over blowpipe or in a muffle. The product is Al_2O_3.

Chromium, as sulphate or other salt, chromalum, may be treated in a precisely similar manner. (See Chromate Reduction.)

Oxidations or Reductions.

In a good many cases before the actual precipitation of a substance in a weighable form can be done, some operation, as "oxidation," has to be performed, and in others again a lower state of oxidation is more convenient for gravimetric work, so that a "reduction" is necessary.

Ferrous salts give good instances where oxidation is necessary, as few complete precipitants of ferrous iron are known. This is the case for other elements as tin, sulphur, phosphorus, silicon, &c.

Iron is generally precipitated as ferric hydrate, and this converted into Fe_3O_4 by intense ignition.

As an exercise, either metallic iron may be taken or ferrous ammonium sulphate. In either case oxidation is necessary before precipitation.

Ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 6H_2O$, is an excellent example for exercise. It contains, when pure, exactly one-seventh of its weight of iron, $392/56 = 7$.

The salt is made by mixing ordinary ferrous sulphate with an equivalent of ammonium sulphate, and dissolving in boiling water containing a very little sulphuric acid. The concentrated solution should be cooled rapidly by placing the vessel in cold water, and shaking or stirring vigorously as before described. The crystals then formed are very small, and may be drained very completely from the liquid by placing in a glass funnel, the apex of which is lightly plugged with asbestos, or even cotton wool.

This should be recrystallised from hot water, and similarly treated whilst cooling. The crystals are finally dried by placing between several layers of blotting-paper.

Take about 1 grm. of the salt for analysis; place in beaker direct from the weighing-bottle; add 20–25 cc. dilute sulphuric acid; warm gently, and then drop in carefully 5 cc. strong nitric acid. A rather violent action may take place, with evolution of nitrogen oxides. Heat to boiling point for a few minutes until all gases have escaped, and add, carefully, ammonia in considerable excess. Allow to boil for 5′, and then filter. Wash the precipitate, which should be bright red, with hot water, and get it well into the apex of the filter, until

the wash-water gives no further reaction for ammonia, or ceases to leave a residue when a drop is evaporated on a glass plate.

Dry the precipitate in the oven; it will contract and detach itself from the paper if washed properly. Place in crucible, either porcelain or platinum, fold up and burn the paper, dropping the ash on to precipitate and crucible, and ignite strongly with the blow-pipe. If made really very hot for some time (20′) it will become Fe_3O_4. This precipitate may also be placed damp into a crucible, preferably of porcelain and ignited directly in the muffle.

If only just heated to redness it will be Fe_2O_3, which requires a really very high temperature for conversion into Fe_3O_4.

This method of treatment does not separate iron from Al or Cr, but to a great extent from Ni or Co and Zn, if they are not in very large amount. From Mn it is only a poor method of separation, unless repeated many times.

Sulphur is mostly converted into sulphuric acid and this again into barium sulphate, $BaSO_4$, whenever sulphur has to be estimated quantitatively as well as recognised qualitatively.

Barium sulphate has several properties which recommend it for this purpose. It is heavy, extremely insoluble in all solvents, easily washed free from adhering bodies, and may be heated to a very high temperature. As an exercise take any one of the sulphides made from the metals (see *ante*, Metals), say the copper sulphide,* pound it up finely and weigh out about one grm. as previously described, and put in a flask or a beaker glass with a cover; pour over it 10 cc. water, and then the same volume of strong nitric acid, and add *one or two* crystals of potassium chlorate, $KClO_3$. Heat gently until all visible action has ceased, and a clear bright green solution results. Dilute with hot water so that the total bulk does not much exceed 200 cc., heat to boiling, and then add barium chloride solution gradually, until no more white precipitate forms. Keep boiling or nearly so for 15′, when the precipitate will have settled. In the meanwhile prepare a filter paper by folding and fitting it well in the funnel and wetting it with hot water. Now pour the clear and hot liquid above the precipitate of $BaSO_4$ carefully through the filter and finally wash out the precipitate *thoroughly* by means of the fine jet of the wash-bottle from the beaker or flask, so as to obtain *every visible particle* on to the paper, and leave the beaker *quite* clean inside. In case of any precipitate adhering to the beaker a glass rod with a piece of tight fitting black rubber tube, about one inch long, at one end should be made. With this the sides of the beaker can be thoroughly rubbed down so as to loosen all the precipitate. Pour hot water five or six times through the filter, permitting to drain, but not get dry, between each washing. Finally wash twice with methylated spirit,

* Gunpowder is an excellent material to try this method on and gives good results with most moderate care. A sample of gunpowder should be powdered up, and the mean results of several students' work taken as the standard, for as it is a mixture every sample will vary in composition.

which takes the water from the paper, and precipitate; allow to dry in the air; lift carefully by the top edges from the glass funnel, place in a crucible, either platinum or porcelain, and *heat directly over a good Bunsen, or in a muffle*, until the residue is perfectly white. The hotter the flame the better, as the moisture in the precipitate and paper will then assume the spheroidal state, and evaporate quietly. The lid must not be on at this time of heating,

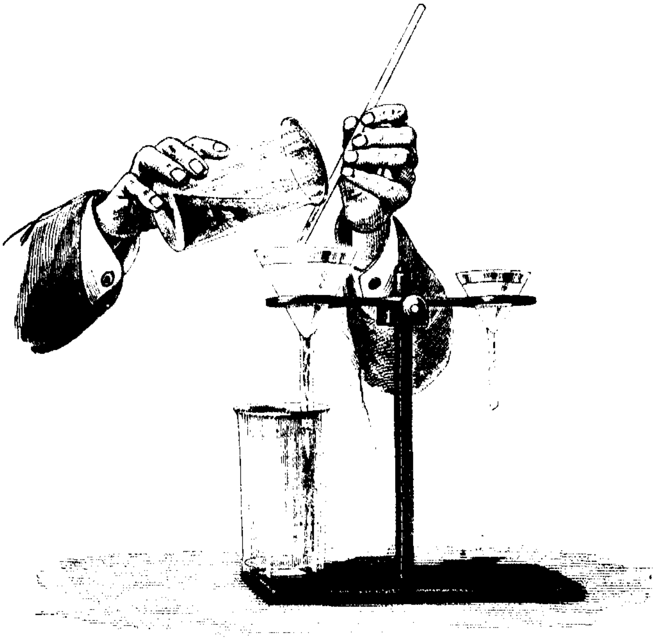

FIG. 29.

but should always be weighed with the crucible, and must be put on before the crucible is carried from the heating operation to the balance. The paper will burn away completely, leaving the ash with the precipitate.*

This method is applicable to gunpowder, and other mixtures containing sulphur, and to most metallic sulphides or sulphites. With

* Generally when $BaSO_4$ is heated in this way with the organic matter of the filter a small quantity of sulphide, BaS, is formed. This will oxidise on long heating in the muffle, but it is best *under all circumstances* after the precipitate has been burnt to whiteness to remove from the flame, or muffle, and add *one or two* drops of strong H_2SO_4, replace in the muffle, or heat over the flame until again red hot. If done in a platinum crucible there is no danger from loss by spirting. A porcelain crucible is not advised for this operation.

sulphates the process is precisely the same, but, of course, the preliminary oxidation is unnecessary.

Example (actual; part of complete analysis of copper sulphate):

Bottle and copper sulphate .	23·5020	Barium sulphate and ash and crucible	= 21·4934
" " " .	21·4930	Crucible . . .	= 19·6107
Copper sulphate . .	= 2·0090	Ash . . .	= ·0030
			1·8797

With the exception of the treatment by nitric acid, all the operations were performed as above described.

As 233 $BaSO_4$ = 32 S ∴ 1·8797 contain ·2581 S.

$\frac{\cdot 2581 \times 100}{2\cdot 0090} = 12\cdot 85$ S per cent. The formula $CuSO_4.5H_2O$ demands 12·83 per cent., or as SO_3 = 38·53 per cent.

TIN.—Very few salts of tin are known excepting the halogen salts and double salts with alkaline haloids. Tin, antimony and arsenic are oxidised by strong nitric acid without nitrates being formed. Arsenic and antimony form acids and tin gives a complicated hydrated oxide, probably $Sn_5O_5(HO)_{10}$. It is quite insoluble in water and HNO_3, and on ignition becomes SnO_2.

The metal or some definite alloy (bronze coinage) should be used as exercise. Not more than 1 grm. of the metal and not more than 3 grms. of a bronze coin need be taken. It should be in filings or clippings. Clean, dry, weigh and place in flask of about 500 cc., pour on 5 to 20 cc. strong nitric acid through a small funnel placed loosely in the neck of flask, then an equal bulk of warm water. A violent action will generally commence. The funnel is to prevent any spirting of liquid from the opening of the flask. When all metal has dissolved, dilute with about 50 to 100 cc. hot water. Boil for 5′, and then filter. Wash the white precipitate, after the acid has drained away, with hot water, until all soluble salts are removed, testing by evaporating a drop on a plate.

The precipitate may be dried, detached from paper and ignited in a porcelain crucible as with CuO, and, or simpler, placed, moist, after draining for a short time, into a porcelain crucible, and heated at once either in the muffle or over the blowpipe. The crucible must *not* be covered if the ignition be done this way, but the lid must be weighed with the crucible and put on after ignition. The product after ignition is SnO_2. It should be quite white. In the case of a bronze coin considerable pains must be taken in the washing, as copper and lead are liable to be retained.

CHROMIUM compounds may be either chromates or salts of Cr_2O_3.

Chromates are generally reduced to chromium salts and the oxide precipitated from these as $Cr_2(HO)_6$.

As an example take potassium bichromate, $K_2Cr_2O_7$.

Twenty or 30 grams of the salt should be purified by recrystallising from hot water (as described under previous salts). It is not very soluble in cold water, and can be very easily obtained in a state of great purity. The crystals from water are anhydrous, but liable to enclose water mechanically. The recrystallised salt must be just melted in a dish or crucible.

On cooling it breaks up into small crystals. Put these in the weighing-tube or bottle; weigh and then shake out a small quantity into a 500 cc. beaker, weigh bottle again. Not more than ·5 grm. need be taken, and certainly not more than 1 grm.

Dissolve in hot water, add 5 cc. strong HCl, heat nearly to boiling, and add 2 to 3 cc. absolute alcohol, cover the beaker with a clock glass and allow to boil. The colour will change from orange to green, and a strong odour of aldehyde will be noticed. The reduction should be complete after the odour of aldehyde has ceased.

Add slowly a few ccs. strong ammonia, keeping up the heating. A grey green precipitate should form. Filter as hot as possible and wash very thoroughly with hot water. It is an advantage if this operation of precipitation and filtration be done quickly, as chrom-ammonias are liable to form on long exposure to air. This will be seen by the filtrate becoming purple. It should be perfectly colourless. It cannot be too well washed.

The filter paper and precipitate may be introduced at once, after draining, into a platinum crucible, and heated either in a muffle or by a blowpipe-flame. The final result is Cr_2O_3, which should be dark green in colour and a perfectly loose powder.

Instead of alcohol, a sodium thiosulphate solution, or yellow ammonium sulphide, or sodium sulphite may be used for the reduction. Some sulphur is thrown down from the former of these, but it does not interfere, being burnt off in the ignition. It is, however, more difficult to filter. The mode of calculation will be evident.

CALCIUM.—Iceland spar is a very pure form of the carbonate, but sometimes contains a little silica, SiO_2. The most complete precipitant for calcium is oxalic acid or ammonium oxalate, in alkaline, ammonia, or acetic acid solution.

Pound up some Iceland spar, place in weighing bottle, weigh, take out into a 500 cc. beaker between ·5 and 1 grm., add about 20 cc. dilute HCl, and 50 cc. water, warm gently until completely dissolved. (If there be any visible residue of silica it will be necessary to filter.) To the perfectly clear solution add ammonia (which should cause no precipitate), and then oxalic acid, still keeping the ammonia in excess. CaC_2O_4 forms, and if the temperature be kept about 60° to 80° C it settles down rapidly, and can be easily filtered and washed with water. The precipitate is best ignited in a platinum crucible over the blowpipe for 30 to 40 minutes, the residue is then quicklime, CaO. The crucible should be uncovered at first until all the paper has been burnt, and for the final 10 or 15 minutes covered with the lid.

BARIUM.—The estimation of barium is practically identical *with that of sulphuric acid.*

With the exception of the chloride, acetate and nitrate, not many of the common salts of barium are soluble. Many organic salts are soluble; for instance, most sulphonates of benzene derivatives.

An excellent exercise with barium is to decompose the sulphate by fusion with a carbonate and reconvert the barium into sulphate, and the sulphuric acid into barium sulphate.

Barium sulphate as heavy spar can be obtained, as a mineral, in a state of almost absolute purity. Grind to fine powder and sift through a gauze sieve. Weigh a platinum crucible, then introduce ·5 to 1·5 grm. of the mineral, cover with at least 5 times as much fusion mixture, which need not be weighed; stir the mixture with a platinum wire, heat up to fusion over a Bunsen flame for about 20 minutes. Cool; place crucible in beaker in about 300 cc. water. The fused mass will partly dissolve and detach from crucible. Wash the crucible free from any adhering salts and filter the solution, and wash the barium carbonate thoroughly and quickly. The filtrate contains the sulphuric acid as sodium salt. This carbonate may now be dissolved off the filter paper by dilute HCl poured through hot and in small quantities at once, and reprecipitated as $BaSO_4$ by the addition of a slight excess of dilute sulphuric acid. The solution should be heated, and, in fact, the whole operation carried out exactly as given under sulphur as barium sulphate (p. 263).

The carbonate of soda solution containing the sulphate is made acid by carefully adding dilute HCl, heated to boiling and slight excess of barium chloride solution added. The $BaSO_4$ is treated as before. The two amounts of barium sulphate obtained should be theoretically equal and practically differ only in the fourth decimal place.

MAGNESIUM. — Most magnesium salts are soluble and resemble zinc salts to a great extent. About the least soluble salt is the double phosphate of magnesium and ammonium, NH_4MgPO_4, which is almost insoluble in water and practically quite insoluble in dilute ammonia, but very soluble in acids.

Magnesium sulphate, $MgSO_4,7H_2O$, or magnesite, $MgCO_3$, or even metallic magnesium, are suitable for exercise; ·2 to ·3 of metallic magnesium will be sufficient, and not more than 1 grm. of the salts. Dissolve the metal in dilute HCl in a small 300 cc. beaker, covered, add sodium hydrogen phosphate in slight excess—no precipitate should form if sufficient HCl be present. Warm gently but do not boil, and add ammonia until the solution smells strongly. Arrange that there is not much more than 200cc. of liquid. Keep in a warm place for a few hours, avoid stirring after adding the ammonia. The precipitate will settle down more or less crystalline. Filter whilst warm, 40° to 60° C, and contrive to wash the precipitate from the beaker with some of the clear filtrate from the first portion poured in. Finally, wash with small quantities of dilute ammonia so that not more than 100 cc. are used.

Allow to drain and pour alcohol twice over the precipitate. Place funnel and precipitate in the steam oven and allow to dry thoroughly.

Weigh a porcelain crucible and lid. When the $MgNH_4PO_4$ is quite dry it will detach almost completely from the paper by very slightly rubbing or pressing the sides of the filter paper cone together. Do this over a piece of clean, smooth, blue writing paper. Drop as much as possible of the substance into the crucible and carefully brush any adhering particles from the filter paper and any that have fallen into the blue paper also into the crucible, using a small camel's hair brush.

The filter paper must then be folded up, coiled in platinum wire, and burnt separately (see Fig. 28), and the ash dropped into the crucible. The crucible, covered, may now be ignited in the muffle, or, gently, over the Bunsen flame. The salt becomes $Mg_2P_2O_7$, molecular weight 222, from which the Mg can be calculated.

This is really a very difficult exercise, and great attention should be paid to details. If it should stick on the sides of the beaker during formation it may be necessary to redissolve in HCl and again precipitate. The pouring rod should *not* be in the beaker at the time, nor should it be stirred, and the beaker *must* be perfectly clean when commencing. The NH_4MgPO_4 is very light and inclined to dust when dry, so care must be taken in getting it into the crucible. A platinum crucible must *not* be used.

POTASSIUM AND AMMONIUM.—The only reliable gravimetric method of estimation of these bases is to convert their salts into the chloroplatinate, K_2PtCl_6, or $(NH_4)_2PtCl_6$, both of which are extremely insoluble in strong HCl, or in alcohol or ether, or a mixture of the two latter.

As potassium and ammonium salts are soluble all other metals can easily be separated from them.

Potassium chloride should be taken for exercise first.

The salt is to be dissolved almost to saturation in hot water, and this saturated with HCl gas and cooled at the same time. The KCl crystallises out with some HCl. It is to be drained from the acid and then melted in a platinum crucible. Some of this salt is pounded up and placed in the weighing bottle. It is deliquescent. Take about ·2 to ·5 grm. in a small porcelain dish, dissolve in about 20 cc. water, or less if possible, acidify with HCl and add platinum chloride in considerable excess. (The strength of the PtC_4 solution should be known.) The whole is then to be evaporated to dryness on a steam or water bath; the residue is K_2PtCl_6 and the excess of H_2PtCl_6 which undergoes partial decomposition into $PtCl_4$. To this one or two drops of HCl are added and allowed to moisten the residue. A mixture of equal volumes alcohol and ether is then added, the residue stirred up with a glass rod and then allowed to stand a few minutes, the dish being covered with a glass plate.

In the meanwhile, whilst the salt solution has been evaporating, a small filter paper has been dried carefully in the steam oven and

weighed. For this a paper must be selected and placed in oven for 30′, it is then put inside a test-tube "carrier" made out of two test-tubes, one of which slides moderately easily in the other (plenty of these "fitting" tubes are to be found in every box of test-tubes). The rim around the open end of the smaller tube is removed, by filing it around and warming in a very small flame. The open end of the smaller tube is then pushed into the larger. This makes a sufficiently air tight carrier for paper and other hygroscopic substances whilst weighing (Fig. 30). The paper must be dried and weighed and dried again and weighed until the two last weighings are the same. The paper must be moistened with alcohol before commencing to filter the potassium salt. A mixture of alcohol and

FIG. 30.—Fitting test-tubes for carrying filter papers, &c. &c., for weighing.

ether should be used to wash all the K_2PtCl_6 on to the paper from the dish and also on the paper, until it comes through colourless and leaves no residue on evaporation. (The filtrate containing the excess of $PtCl_4$ is saved.)

The funnel and paper are placed in the oven to dry and then in the carrying tubes to weigh. The drying and weighing must be repeated until the weight is constant.

The difference between the weight of the carrier + paper and carrier + paper + K_2PtCl_6 evidently gives the weight of the latter.

It is possible to get a check on this by decomposing the double salt into metallic platinum and KCl. K_2PtCl_6, when ignited in a muffle for a long time, preferably in a weighed platinum crucible, gives 2KCl + Pt + chlorine, which escapes. Generally the platinum is so coherent that the KCl may be washed away with warm water and the Pt left. After again heating the crucible can be weighed and the potassium equivalent calculated from the weight of platinum.

AMMONIUM.—The method for potassium applies exactly to ammonium, excepting that it is not necessary to weigh the $(NH_4)_2PtCl_6$ in the dried filter paper, although it is advisable to do so.

After getting on the filter paper and washing, as with potassium, the filter paper and salt can be placed at once in a weighed platinum crucible, covered with the lid and heated, gently at first, over a Bunsen flame; when gases have ceased to escape the lid may be removed and the carbon, from the paper, thoroughly burnt off. Platinum only should be left. One atom proportion of Pt = 194·34 is equivalent to $2(NH_4) = 36$.

SODIUM.—Properly speaking there is no insoluble sodium compound that can be used for gravimetric determination. Many salts,

such as the nitrate, chloride, acetate, &c., when heated with H_2SO_4 are converted into sulphate, the more volatile acid being driven off.

Supposing the sodium salt to be one with a volatile acid; weigh a platinum crucible and lid, introduce about ·5 grm., not more, of the dry salt, support on a triangle, add a few drops H_2SO_4, arrange the lid and conduct the operation as in Fig. 27 (p. 255).

In case the sodium is combined with a non-volatile acid as phosphoric, it will generally be possible to effect a double decomposition, say,

$$Na_2HPO_4 + MgSO_4 + NH_4OH = MgNH_4PO_4 + Na_2SO_4.$$

The filtrate here will contain Na_2SO_4 with some $MgSO_4$, on evaporation to dryness and heating to redness some of the $MgSO_4$ will be decomposed. On dissolving residue in water and filtering there will still be Mg present. It may be removed either by $Ba(HO)_2$ solution or freshly precipitated and washed HgO, the filtered solution being again filtered and then evaporated to dryness, taken up with dilute H_2SO_4, filtered and finally evaporated and ignited.

HALOGENS.—The amount of halogen in any haloid salt can be determined by precipitating the halogen (Cl, Br, or I) with silver nitrate in the presence of a little nitric acid, in which the silver haloid is quite insoluble. A few metal salts of halogens, as those of lead and copper and mercury, are somewhat insoluble or quite insoluble in water, but dissolve either in acids or alkalies.

Example (actual) with sodium chloride.

A sample of common salt which had been recrystallised twice from strong hydrochloric acid, and then heated in a platinum crucible to melting, was powdered and placed in a small weighing bottle.

Bottle and salt	8·9748
Poured some salt into beaker, weighed bottle again .	8·1685
NaCl taken	0·8063.

This was dissolved in 50 cc. hot water in the beaker into which it was put from the bottle. 1 cc. nitric acid was added, and then a solution of nitrate of silver added slowly, as long as a precipitate formed; heated to boiling, and then a few (5) cc. silver solution added to make sure there was an excess; filtered hot through a folded filter paper, and washed with hot water containing 1 cc. deci-normal nitric acid in 500 cc. (this quantity of water, if used in repeated small doses, will be found sufficient to wash this weight of precipitate perfectly); it was then dried in an oven, detached from paper; placed in crucible; paper burnt, and ash dropped in, and then the crucible and contents heated nearly to the melting point of the chloride of silver.

Weight of porcelain crucible and precipitate and ash .	24·8513
" " crucible	22·8800
Ash	·0045
AgCl	1·9668

As 108 parts of silver unite with 35·5 of chlorine and only one halogen (chlorine) compound of silver is known, the proportion of chlorine in common salt can be calculated from the amount of silver chloride formed:

$$\frac{\overset{Cl}{\overline{35 \cdot 5}} \times \overset{AgCl}{\overline{1 \cdot 9668}} \times 100}{\underset{AgCl}{\underline{143 \cdot 5}} \times \underset{NaCl}{\underline{\cdot 8063}}} = 60 \cdot 35 \text{ per cent. Cl.}$$

Calculated from the formula NaCl, Cl = 60·68 %.

In doing these haloid salts of silver it must be noted that, if any adhere to the filter paper, it will be reduced more or less to metallic silver as the paper is burnt. If it be then mixed with the haloid salt in the crucible, and weighed as such, there will evidently be something wrong. It is not always safe to take it that the silver salt adhering to the paper is perfectly reduced. This may be the case when the paper has been very tightly rolled up before burning, so that H and CH_4* come well into contact with it. If even somewhat loosely bound up, the amount of reduction is very variable; a far better plan is to put ash into crucible as above described, and then, whilst heating, treat the precipitate with a little of the particular halogen of which it is the salt.

With iodide there is no difficulty; simply add a small crystal of iodine whilst heating up. With bromide, either a drop may be put into the crucible, or better, before heating up moisten the precipitate with a solution of bromine in ether, and allow to evaporate before heating to fusion. With chlorides, the simplest way to ensure complete chlorination is to blow a little chlorine gas into the crucible *during the heating*. A test-tube with cork and ⊏-shaped delivery tube is needed. About a grm. of potassium permanganate crystals are put in the test-tube, and a couple of cc. of strong HCl added immediately before using. The chlorine is directed into the crucible containing the silver chloride by means of the bent tube. Take care the chlorine is not coming off too vigorously or it may blow out some of the paper ash, but generally there is no danger of this with the amount of permanganate named.

CARBON AND HYDROGEN.—Compounds of carbon and hydrogen require somewhat special methods and apparatus for their quantitative analysis. Carbon and hydrogen in minerals are mostly as CO_2 and H_2O, which may generally be determined by difference, either by heating alone, or by treatment with some non-volatile acid. (See p. 253.) In organic substances C and H are best determined by a combustion process. (Carbon in irons and steels may also be determined by this process.)

In this combustion process the carbon is converted into CO_2, and the hydrogen into H_2O, in such manner that both products may be caught and weighed separately.

* These two gases are decomposition products of cellulose or paper.

As CO_2 contains carbon to the extent of 12 in 44, and H_2O 2 of H in 18, the weights of C and H corresponding to the CO_2 and H_2O can readily be found.

The actual operation is carried out in a glass tube, through which purified dry air or oxygen can be driven. In this tube a weighed amount of the substance is heated, and "completely" burnt.

The substance, if a solid, or a liquid of not very volatile nature, may be contained in a "boat" of platinum or of porcelain. If very volatile, then a special tube must be employed.

The actual requisites are:

I. A "tube furnace," which may be simply a row of Bunsen burners (20–30), mounted in a frame, so that a tube of 24–30 inches length can be heated to redness. If the laboratory be supplied with such furnace no figure is required. Without one the ordinary "combustion" analysis cannot be done.

II. A glass tube about $\frac{5}{8}$ inch clear diameter, and about 4 inches longer than the furnace. It must be of difficultly fusible glass.

III. An air-aspirator of some kind. A Bunsen waterfall pump is convenient. The simplest is a two or three gallon bottle or jar, with an opening near the bottom fitted with a tap. A cork with small

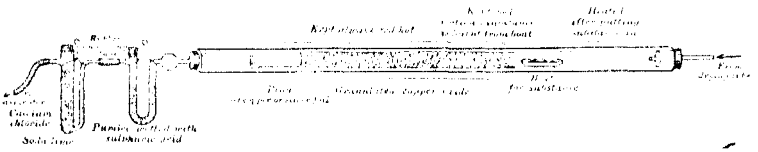

FIG. 31.

tube is fitted to the neck. When the bottle is filled with water, and the tap opened, air is aspirated or drawn in through the top tube to take the place of the escaping water.

IV. A drying and purifying arrangement for the air before it enters the tube. The simplest and most effective consists of a tube about 20 inches long and about 1 inch diameter, with corks and small tubes at each end, and charged with coarse soda-lime. The air is drawn through this first, and then bubbles through concentrated sulphuric acid contained in a small two-necked bottle. Small glass and rubber tubes are used for connections. From the sulphuric acid bottle the air passes into (V.) the combustion-tube. This should be charged with copper oxide, as shown (Fig. 31). It must be "granular" oxide, made from bits of wire.

VI. The absorbing apparatus first attached directly to the combustion-tube—a U-tube charged with pumice-stone moistened with strong sulphuric acid.

2nd. A similar tube, with dry soda-lime, or better, a tube as seen in Fig. 31, made from a common test-tube, and charged, the bottom three-quarters with soda-lime, and the top quarter with dried calcium chloride, just separated by a thin plug of cotton wool.

The end of this tube is attached by rubber tube with a small U-tube containing H_2SO_4, to serve as indicator and then the aspirator arrangement.

The two tubes are weighed separately, and then attached to the tube as shown. (See Fig. 31.) The boat is then weighed, the substance introduced, and weighed again. It is usual to carry the boat in a small corked tube; or better, fit one test-tube into another (see Fig. 30), so that one tube acts as a cap to the opening of the other. The boat and contents are thus protected from loss or gain in transit from the balance to the tube. The tubes are only for carrying the boat, and are *not* put into the combustion-tube and not necessarily on the balance-pan.

After the substance and boat are introduced, the burners *behind* the boat are lit, and as the heat reaches the substance it should gradually either distil into the portion of copper oxide kept cool, or decompose and slowly burn.

Considerable judgment is necessary in conducting this operation. Some bodies may be heated up much more quickly than others, and no rule can be laid down, excepting that a volatile substance must have more time and less heat applied behind the boat at the commencement. There is no particular sign when a combustion is ended and the CO_2 and H_2O swept completely from the tube. It is therefore customary to continue the process for some time after all the substance has gone from boat and tube, and allow time for mixing and sweeping out of the gases.

After the substance has burnt from the boat, and the whole tube has been heated to redness, the tube may be finally cooled by turning off the burners at the end where the air enters, and as far as the main bulk of copper oxide. When the combustion appears over, the two tubes, in which water and carbonic oxide have been collected, are separately detached and weighed.

If the drying and purifying apparatus for the air be in proper order, no harm will result from keeping on the operation long after the combustion is really complete, but generally speaking an hour and a half is sufficient.

The weight of substance taken should have some connection, if possible, with its carbon contents, as it is advisable to have a good margin of excess of soda-lime over the CO_2 to be absorbed. From ·2 to ·5 grm. substance is mostly sufficient. As an example, actual:

·1250 substance:

$$\text{gave } H_2O = \cdot 0748.$$
$$CO_2 = \cdot 3887.$$
$$\frac{\cdot 0748 \times 100}{9 \times \cdot 1250} = 6{\cdot}65 \text{ per cent. H.}$$
$$\frac{\cdot 3887 \times 3 \times 100}{11 \times \cdot 1250} = 84{\cdot}8 \text{ per cent. C.}$$

This calculates to the formula $C_{13}H_{12}O$ = H6·58; C84·78.

In most compounds oxygen is still "taken by difference." That

is, all the other elements are actually found, and the difference from 100 taken as the amount of oxygen, if that element is found by qualitative examination to be present.

A method of combustion in hydrogen has been proposed, but for most cases it is quite unnecessary to have a direct determination of the oxygen, there being no doubt, from other evidence.

NITROGEN.—The most generally applicable method of determination of the amount of nitrogen depends on the fact that most nitrogenous substances when heated with soda-lime (a mixture of CaO with NaHO) yield the whole of the nitrogen in combination with hydrogen as ammonia. This applies strictly to all compounds where the nitrogen is *not* directly united with oxygen.

Nitrates and nitro-derivatives, where the nitrogen is *more or less* "oxidised," require a considerable modification of this treatment.

Nitrates, whether mineral or organic, and both nitric and nitrous acid solutions, are best analysed in the "nitrometer."

Nitro-compounds, as picric acid $C_6H_2(NO_2)_3OH$, and some amino

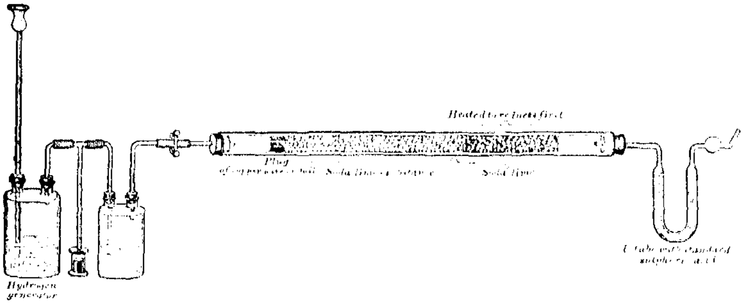

FIG. 32.

and imido compounds, are best analysed by combustion with CuO in a vacuum tube connected with a Sprengel pump so that the nitrogen is collected and measured.

The same treatment is necessary with some other classes of nitrogen compounds, but modifications are necessary in some cases. Where the substance is an explosive, for instance, picric acid mentioned above, would need to be mixed with either fine sand or starch to modify its "decomposition" sufficiently to be safe.

When the nitrogen is determined as ammonia, the operation can be conducted in a piece of "combustion" tube 14–18 inches long and open at both ends, and so arranged that a stream of hydrogen can be continuously passed through.

The tube is heated in a furnace as with the carbon and hydrogen determination.

The hydrogen requires to be washed by passing through water, and then a potassium hydrate solution, but need not be dried.

The figure explains arrangement of tube and charge.

The substance, if a solid, is weighed in a weighing bottle, a small quantity, about ·5 to 1 grm. shaken out into a small dish or mortar and the bottle weighed again. The quantity shaken out is then *mixed by means of a wire with a few grms. of dry but cold soda-lime*, and by means of a smooth paper gutter introduced into the tube, as will be evident by Fig. 32. There is a plug of copper-wire or foil in the front of the tube; then a layer of about two inches of soda-lime only. The mixture of substance and soda-lime comes after this. The dish or mortar is washed out by more soda-lime, until the tube is nearly full. An excess cannot hurt.

Another copper wire, or an asbestos plug, keeps the soda-lime in place at this end. This end of the tube has a moderate-sized **U**-tube *fitted to it with cork. The* **U**-*tube contains a quantity of either* H_2SO_4 or HCl of known strength. (Standard acid.)

The ammonia produced in the tube neutralises *some* of the acid. The strength and quantity of acid being known beforehand, the amount actually neutralised by the ammonia can easily be found. The hydrogen is permitted to flow slowly through the tube during the whole time of heating, so as to convey the ammonia as fast as formed into the acid.

The determination of the amount of ammonia by the use of an acid of known strength comes under "volumetric" analysis.

After charging the combustion-tube with the substance and soda-lime, the **U**-tube, to be fixed at the end, is charged with an accurately known quantity of the acid, and then attached.

After the combustion is ended the acid is carefully emptied and washed from the **U**-tube into a dish, a few drops of litmus added, and then the soda solution as with the process of matching it with the acid. *See acid and alkali (page 283) et seq. If, say, 25 cc. of* $\frac{N}{10}$ acid were employed in the tube and it required only 20 cc. of the soda solution, then the difference, 5 cc., must have been neutralised by the ammonia liberated in the combustion-tube.

With a solution of $\frac{N}{10}$ strength each cc. = ·0049 acid, or ·0042 soda, or ·0017 NH_3, or ·0014 N. So that in the case imagined the amount of nitrogen would be 5 × ·0014, evolved in the form of ammonia.

Nitro derivates may be analysed by this method when mixed with five or six times their weight of starch. It is more usual, however, to burn them with copper oxide in a Sprengel vacuum, and collect the nitrogen gas over strong soda solution, which absorbs the CO_2 formed by the carbon burning. The water produced does not interfere.

The method of combustion with CuO in a tube attached to a Sprengel pump by which the gases are pumped out and measured, is one of the most accurate methods of analysis devised, and can be employed not only for nitrogen but for carbon as well.

VOLUMETRIC ANALYSIS.

The object of volumetric analysis is to ascertain, quantitatively, the composition of a given substance by means of solutions of a reagent of known strength. Certain characteristic reactions are produced, and from the *quantity* of reagent used, the amount of substance present may be deduced from the laws of chemical equivalence. All that is necessary for the successful performance of the analysis is that the exact termination of the reaction shall be made visible.

As will be seen subsequently, the apparatus required in volumetric processes is of a much simpler character than that employed for gravimetric analysis. In addition, the estimation may be performed very rapidly, and with an accuracy quite equal to that obtained by the most careful gravimetric methods, and in some cases even more so.

End of Reaction.—As previously mentioned, the success of any volumetric analysis depends upon the termination of the reaction being definite and observable. The most general methods of ascertaining this may be classified as follows:

1. *The appearance or disappearance of a distinct colour in the liquid under operation.*—An example of this is to be found in the estimation of iron salts by potassium permanganate. If the permanganate solution be added drop by drop to an acid solution of a ferrous salt, the colour is discharged so long as the latter is in excess. When the permanganate strikes a distinct colour in the liquid the oxidation of the ferrous salt has been completed. Conversely, when hydrogen peroxide is added to a solution of permanganate, the colour of the latter becomes fainter and finally disappears at the moment the reaction is complete. In both cases the final change is brought about by one or two drops of solution, which may be extremely dilute.

2. *When a precipitate just ceases to form.*—An example of this is afforded by a well-known method of estimating silver. If a solution of sodium chloride be gradually added to a silver solution, the latter being constantly shaken so as to allow the precipitate to subside, a point will be reached at which a drop of the salt solution ceases to cause a further precipitation. This indicates the end of the reaction.

3. *By the use of an indicator*, which may be defined as a substance which renders the end reaction evident, without itself interfering with the reaction. Examples of these are provided by the

estimation of the acidity or alkalinity of a given solution; and as this is one of the most frequent uses of volumetric analysis, the names and properties of the chief acid and alkali indicators will be given:

(*a*) *Litmus.*—The solution of litmus, as is well known, is turned red with an acid and blue with an alkali. If one be added gradually to a solution of the other, into which a little litmus has been poured, a point of neutrality will be reached when the litmus is neither red nor blue; after which one drop of acid or alkali will turn it red or blue. The end of the reaction is thus made evident. The objection to litmus is that it is affected by carbonic acid, so that in such cases as the estimation of alkaline carbonates with an acid, the litmus is turned prematurely red. Boiling the solution during the process obviates this.

(*b*) *Methyl orange* (para-sulpho-benzene azo-dimethylaniline), is an orange coloured body, soluble in water. It becomes red on the addition of an acid. It should be made by dissolving 1 grm. of the solid in a litre of distilled water. One drop of this solution present in the alkaline liquid will strike a red tint immediately an acid is added in excess. It is probably the best indicator for acids and alkalies, being totally unaffected by carbonic acid or sulphuretted hydrogen.

(*c*) *Phenolphthalein.*—This indicator is prepared by dissolving 5 grms. of the powder in 1 litre of 50 per cent. alcohol. A few drops of this solution show no colour in a neutral or acid solution, but the faintest excess of alkali produces a deep purple-red. It is, however, affected by CO_2 and H_2S.

The indicators used in other volumetric processes are too numerous to classify here; such as are used in the processes to be described will be found, with the principles of their action, in the description of the analyses.

STANDARD SOLUTIONS.—A standard solution may be defined as an arbitrary solution possessing a known chemical strength. Such solutions are generally, though not always, made in accordance with the chemical equivalent of the reacting body, as explained in the next definition.

NORMAL SOLUTION.—A normal solution is one which possesses the hydrogen equivalent of the reacting element in grams in 1 litre. It is generally expressed by the symbol N. Reference to examples will make clear the definition given.

1. Sodium hydrate, NaOH, contains 23 parts by weight of sodium; 23 being the hydrogen equivalent to 16 of oxygen and 1 of hydrogen. A litre of normal sodium hydrate would therefore contain 40 grms. $(23 + 16 + 1)$ of NaOH = 23 grms. of sodium.

2. Sodium carbonate, Na_2CO_3, contains 46 parts by weight of sodium, or two equivalents. For a normal solution we must therefore divide the weight expressed by Na_2CO_3 by 2, which will give the amount in grams to be contained in 1 litre.

3. Copper sulphate, $CuSO_4$, contains 63 parts by weight of copper. The hydrogen equivalent of copper is 32·5, since copper is

divalent. The number of grams in a litre of normal copper sulphate is therefore *one half* of the *number represented* by $CuSO_4$.

It is of great importance that this point should be clearly understood, in order that a thorough insight into the various volumetric processes may be obtained.

The chief advantages obtained by making standard solutions of normal strength are that any two such solutions, capable of reacting upon each other, do so *in exactly equal volumes*, and that the final calculations are rendered much easier.

It is often an advantage to employ solutions of less strength than normal, in such cases they are usually made some simple fraction of normal; thus deci-normal ($\frac{N}{10}$); semi-normal ($\frac{N}{2}$), &c.

All standard solutions should be kept in well stoppered bottles. Before using for an analysis they should be well shaken, as evaporation from the surfaces of the liquid causes a deposition of water on the sides of the bottle, leaving the remaining solution unduly strong.

Titration.—The actual operation of running in a standard solution to the liquid undergoing analysis, and the observation of the end reaction are expressed by the term "titration." The solution is run in from a graduated instrument, to be afterwards described. By this means the amount of solution used is accurately known. The solution undergoing estimation may be contained in either a beaker, flask or dish. Whichever of these is used it is essential that constant mixing shall take place, in order that every part of the liquid may participate in the reaction. This may be accomplished in the case of a flask by swishing round the contained liquid and then slightly inclining; in open vessels a glass stirring-rod may be used. The instrument from which the standard solution is delivered should never be so far removed from the test liquid as to cause splashing; and the solution should not be allowed to run down the side of the beaker or flask, as difficulty is experienced owing to the adhesion of the solution to the side of the vessel.

The details of the titrations given will be found under the respective headings.

Graduated instruments.—The three chief graduated instruments required in volumetric analysis are the pipette, the measuring flask, and the burette.

The pipette, as shown in the sketch, consists of a narrow piece of tubing widened out at the centre. The bottom portion of the narrow tubing is drawn out to a moderately fine taper point, so as to allow the liquid to be retained when the opposite end is closed, and also to ensure a moderately slow delivery of the contents. The graduation consists of a mark on the upper portion of the narrow tubing.

Pipette.
FIG. 33.

To use the pipette, the point is immersed in the liquid from which an exact volume is to be transferred to another vessel.

AGRICULTURAL COLLEGE

Suction is then applied, using the tongue as a valve, until the liquid rises 2 inches or more above the mark. The forefinger is then rapidly placed over the open end, when, by gently moving the finger, air may be slowly admitted and the column allowed to sink until the bottom of the meniscus is opposite the mark. The finger is then pressed tightly, and the pipette removed bodily and its contents discharged in the receiving vessel by lifting the finger. The last drop remaining in the tapered portion may be expelled by touching it against the side of the vessel closing the top with the finger and grasping the wide portion with the hand. The warming expels the last drop. The pipette is evidently made to *deliver* a given volume; its actual contents are obviously greater, as it is wetted by the liquid and therefore retains a portion on its sides. Before using the pipette for a different solution, it should be rinsed out with distilled water several times, dried, and rinsed out with the new solution before final filling. Care must be exercised during the last stages of filling, otherwise the solution may be drawn into the mouth. A few inches of small rubber tube at the top of the pipette is most convenient.

Convenient sizes of pipettes are 100 cc., 50 cc., 25 cc., 20 cc., 10 cc. and 5 cc.

Measuring flasks may be obtained in various forms and sizes. In preparing standard solutions such flasks are absolutely necessary.

FIG. 34.—Measuring Flask.

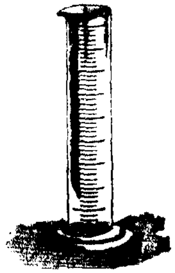

FIG. 35.—Measuring Cylinder.

The flasks are of such a size that the graduation mark may be placed on the neck. The best form is that shown, containing an accurately ground glass stopper; so that any solution contained in the flask may be mixed and preserved from evaporation. The stoppered flask, however, is not absolutely necessary. Such flasks are usually made to *contain* a given quantity; the amount they will deliver is obviously less, and should a flask be used for the latter purpose it must be specially graduated.

Convenient sizes are 1 litre, 500 cc., 250 cc., 200 cc., 100 cc, and 50 cc.

In filling to the mark the last few drops should be blown in from a wash-bottle jet. Where it is only requisite to measure or deliver quantities of liquids roughly, measuring cylinders are used. They consist of cylinders graduated by divisions marked on the side, and should possess a lip for convenience of pouring. Such cylinders are of great service in the rougher portions of the work involved in volumetric analysis.

Convenient sizes are 250 cc. and 100 cc.

The Burette.—There are numerous forms and sizes of this instrument obtainable, but the best form for general use consists of a graduated tube with a tap at the bottom which by careful turning may be adjusted so as to allow only a single drop to escape.

A convenient size for ordinary use is the one graduated in tenths to 55 cc. Two drops are about equal to $\frac{1}{10}$th of a cc. The method of using the burette is as follows: Pour in a few cubic centimetres of the solution to be used, and incline the burette so that every portion is washed in turn by the liquid. This washing liquid is now poured away, and the burette filled to a height of about two inches above the zero mark. It is then clamped in a stand and the tap rapidly turned on full and closed again. This operation expels the air bubble in the tapered tube beneath the tap. The eye is now placed on a level with the zero mark, and the tap gently turned so as to allow a very gradual escape of the liquid. The column falls slowly, and when the bottom of the meniscus is exactly opposite the zero mark the tap is closed. The drop clinging to the bottom is removed by touching with a glass rod, when the liquid to be titrated may be placed beneath the burette. If the amount of solution required for the reaction be approximately known, this amount minus about 2 cc. may be run in at one operation. The final stage of the reaction is found by running in two drops at a time, stirring the solution with a glass rod after every addition. A point will be reached when the addition of a given two drops will cause the indicator to turn colour, at which stage the reading of the burette is taken by observing the mark opposite the bottom of the meniscus, holding the eye level with the mark. When nothing is known as to the strength of the liquid to be titrated, an approximate idea must be obtained by running in 1 cc. at a time, when the end reaction will be found between the limits of a cc. The burette must be again filled with solution, and a second titration performed accurately, the last portions of the solution being run in drop by drop until the reaction is seen to be completed.

When the burette is to be used for another solution, it should be rinsed out several times with distilled water and dried. It may then be rinsed out with the new solution, and filled and run down to the zero mark as before.

The drop clinging to the bottom of the burette during the titration may be transferred to the liquid by touching with the stirring

rod and immersing the latter in the liquid undergoing titration. When the end of the reaction is close at hand, this drop frequently suffices to complete the change of tint in the indicator.

The burette may be filled directly from the bottle containing the solution by holding it vertical, and allowing the lip of the bottle to rest on the top. The solution must be poured in gently, otherwise it will flow over the outside of the burette. With a little care and practice, however, the burette may be filled in this manner without danger of overflowing.

For all ordinary volumetric estimations, it is only necessary that the readings of the burette be taken to $\frac{1}{10}$th of a cc., as this amount is frequently necessary to make the change in the indicator absolutely certain. For more refined methods, Erdmann's float may be used, by means of which readings to $\frac{1}{20}$th of a cc. may be accurately observed. This consists of a weighted glass tube having a mark round its circumference. After roughly filling the burette the float is dropped into the liquid, when the mark will be seen to be below the surface. To adjust the burette for titration the tap is first rapidly and then gradually turned as before, until the mark on the float is opposite the zero mark. The final reading is taken after titration by observing the graduation opposite to the mark on the float.

PREPARATION OF NORMAL ACID AND ALKALI.

A normal acid and alkali are frequently used in volumetric analysis, and their preparation should form one of the first lessons of the student. By accurately following the instructions given, correct solutions may be made by the beginner:

(1) Normal sulphuric acid.

$$\frac{H_2SO_4}{2} = 49 \text{ grms. per litre.}$$

Strong sulphuric acid, as purchased, having a specific gravity of 1·84 at 15° C., has a strength of about 36 times normal; 1 cc. diluted to 36 cc., or 27·8 cc. diluted to 1 litre, would therefore possess a strength approximating to normal.

Place about 900 cc. of distilled water in a litre flask, and pour in 28 cc. of the strong acid, stirring with a glass rod, in order to mix thoroughly. Allow the mixture to become quite cool, lift the rod out of the liquid and wash with a jet of water from a wash-bottle, and add water up to the mark. The mixture should now be poured into a large, dry beaker, and stirred with a glass rod or strip to ensure thorough mixing.

A sample of the solution must now be tested in order to determine its strength accurately. Two methods are here given, both of which should be tried to ensure absolute accuracy.

a. Standardising the acid by precipitation as barium sulphate.—For this purpose 10 cc. of the acid are transferred to a beaker by means of a pipette, diluted with water, heated, and precipitated by the addition of barium chloride. The precipitate is treated as described in the section on Gravimetric Analysis. For the acid to be strictly normal, the weight of the precipitate of $BaSO_4$ should be exactly 1·165 grms., as may be calculated from the equation:

$$H_2SO_4 + BaCl_2 = BaSO_4 + 2HCl,$$

remembering that the weight of real acid in a litre of normal sulphuric acid is one half of that represented by the formula H_2SO_4. Two such precipitations should be performed; if these agree the acid may be diluted or strengthened according to the figures obtained so as to make its strength exactly normal.

Example (actual):

10 cc. of acid prepared as above gave with barium chloride a precipitate weighing 1·1824 grms.
Check 10 cc. gave 1·1818 grms.
Mean = 1·1821 grms.
The acid was therefore too strong in the proportion of $\frac{1·1821}{1·1650} = \frac{1·0147}{1}$. It was therefore necessary to add 14·7 cc. of water to every litre of solution to make the acid strictly normal. After dilution and mixing 10 cc. yielded 1·1642 grms., showing that the acid was as nearly as possible normal.

b. Standardising the acid by means of sodium.—A piece of sodium is freed from naphtha by pressing between the folds of filter paper. It is then cut rapidly with a knife so as to present a perfectly clean surface on all sides, and transferred by the knife to a stoppered weighing-bottle (whose weight has previously been determined), and then weighed. From three-quarters of a grm. to a grm. will be found a convenient quantity for this experiment.

The sodium is now dropped from the weighing bottle into a flask of about 350 cc. capacity, containing about 100 cc. of pure alcohol, in which the sodium dissolves quietly. The flask should be inclined, so that a stream of water may be allowed to run over it while the sodium is dissolving. After the sodium has dissolved, the solution is diluted with its own bulk of water, and a few drops of methyl orange indicator or litmus added. The acid to be tested is now run in carefully from a burette until the indicator just turns colour. The approximate amount of acid required being easily calculated from the amount of sodium taken, one titration will be sufficient if the last two or three cubic centimetres be added gradually. The acid is then corrected to normal by adding the requisite amount of water or strong acid, as indicated by the calculation.

Example (actual):

0·6210 grms. of sodium required 25·8 cubic centimetres of acid.

Check 0·7130 grms. required 29·7 cc.

From the definition of a normal solution 23 grms. of sodium should require 1000 cc. of normal acid, therefore 0·621 should require $\frac{1000 \times 0 \cdot 621}{23} = 27 \cdot 0$ cc.; and 0·713 should require $\frac{1000 \times 0 \cdot 713}{23} = 31 \cdot 0$ cc. The acid was therefore too strong in the ratio of $\frac{27}{25 \cdot 8}$ or $\frac{31}{29 \cdot 7}$ and was diluted by adding 12 cc. of water to every 258 cc. of acid, as indicated by the first ratio. After mixing it was again tried, when 0·658 grms. of sodium required 28·6 cc. of acid, showing it to be strictly normal.

Having obtained an exactly normal acid by the above means, a normal alkali may readily be obtained, as it is only requisite to adjust the strength so that it exactly neutralises an equal volume of normal acid. For a normal alkali either pure sodium carbonate, or sodium hydrate made from sodium, may be used. The former is preferable for many reasons, but suffers from the objection that the solution must be boiled during the titration if litmus be used as indicator, the carbonic acid evolved turning the litmus red before the completion of the reaction. If methyl orange be used as indicator, however, this objection is removed, as the colour of methyl orange is unaffected by carbonic acid. The preparation of normal sodium carbonate will therefore be given.

(2) Normal sodium carbonate

$$\frac{Na_2CO_3}{2} = 53 \text{ grms. per litre.}$$

A quantity of pure anhydrous sodium carbonate is gently ignited in a platinum vessel and allowed to cool; 53 grms. are then accurately weighed and dissolved in water in a beaker. The solution is then transferred to a litre flask, the beaker washed and the washings added, and water then added up to the mark. It is mixed by pouring into a dry beaker and stirring, and returned to the flask. To test its accuracy 50 cc. are measured out in a pipette and transferred to a beaker. About 200 cc. of water are added, and a few drops of methyl orange indicator. The normal sulphuric acid previously prepared is run in from a burette, when exactly 50 cc. should be required. If too strong or too weak, the amount of water or sodium carbonate to be added may be calculated as previously explained.

NOTE.—A beaker of at least 500 cc. capacity should be used for this titration, so as to avoid loss by spirting caused by the evolution of *carbonic acid gas*.

By the aid of a standard acid and alkali a number of useful estimations may be performed by the student. A good exercise is

to find the strength in normals of some of the common laboratory reagents. Thus the strong hydrochloric acid of sp. gr. 1·16, will be found to be about 10 N; the strong nitric acid, of sp. gr. 1·42, 16 N; the strong ammonium hydrate, sp. gr. ·88, 17 N; and so on. Quantities should be taken so as to require about 50 cc. of the standard acid or alkali, so that the operation may be performed without having to refill the burette; such quantities may be calculated roughly by reference to the figures given. A knowledge of the chemical strength of reagents is thus obtained, and the amount required to dissolve any given substance may be easily deduced. For example, if it be required to know how many cc. of strong HCl are required to dissolve 10 grms. of chalk, it is seen from the equation

$$\underset{100}{CaCO_3} + \underset{71}{2HCl} = CaCl_2 + H_2O + CO_2,$$

that 100 grms. of chalk require 71 grms. of HCl = 2 litres of N. HCl. ∴ 10 grms. require 200 cc. of N. HCl = 20 cc. of 10 N or strong acid. The value of such calculations is quite evident.

PREPARATION OF DECI-NORMAL POTASSIUM PERMANGANATE.

$$\frac{KMnO_4}{50} = 3·16 \text{ grms. per litre} = \frac{N}{10}.$$

This salt is not sufficiently soluble in water to admit of a normal solution being used, and a deci-normal solution is found to be most convenient in practice. In calculating the amount of salt that should be contained in such solution, it should be remembered that when potassium permanganate is used as an oxidising agent it is the *available* oxygen which is the reacting element. As this is represented by 5 atoms in the formula $K_2Mn_2O_8$, and as oxygen is divalent, it follows that $\frac{K_2Mn_2O_8}{5 \times 2}$ or $\frac{KMnO_4}{5}$ will be the weight of $KMnO_4$ in one litre of normal solution, and $\frac{KMnO_4}{50}$, = 3·16 grms. is the weight of salt contained in a litre of deci-normal. (See *ante*, Manganese, page 44.)

Dry a quantity of pure potassium permanganate crystals by gently warming, and after cooling weigh out exactly* 3·16 grms. Transfer this to a beaker, dissolve in water, and pour the solutions into a litre flask. The crystals dissolve rather slowly, and it is advisable to pour the first water into the graduated flask after being

* Note that it is sometimes very difficult to weigh out any particular amount of a substance. If 100 grms. are wanted to be dissolved in 1000 cc. water, as nearly 100 grms., say 98·7000, are weighed and then obviously the proportionately *less* amount of water used.

in contact with the crystals for about five minutes, stirring being frequently resorted to. Fresh water is then poured over the remaining crystals; and so on until the solution is completed. The beaker is then thoroughly rinsed out, the washings being poured into the flask, and water added to the mark. Mix as usual by pouring into a beaker and stirring, and returning to the flask.

Standardising the potassium permanganate solution.—The best method of obtaining the exact strength of the solution is by employing ferrous ammonium sulphate, which may be obtained pure. This salt is also convenient for calculation, as it contains exactly one-seventh its weight of iron, as will be apparent from the formula:

$$FeSO_4,(NH_4)_2SO_4,6H_2O$$

the atomic weight of iron being 56. (See also *ante*, page 262.) When acted upon by potassium permanganate in the presence of sulphuric acid, the following reaction takes place (neglecting crystal water):

$$2KMnO_4 + 10Fe(NH_4)_2(SO_4)_2 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + 2MnSO_4 + 10(NH_4)_2SO_4 + K_2SO_4 + 8H_2O.$$

From the above equation it will be seen that $2(KMnO_4)$ or 316 grms. of permanganate react with $10 \times 56 = 560$ grms. of iron; therefore 3·16 grms., or 1 litre of deci-normal solution, would react with 5·6 grms. of iron, and 100 cc. would react with ·56 grms. of iron. The weight of ferrous ammonium sulphate containing this quantity of iron is $·56 \times 7 = 3·92$ grms. Weigh out about 1·5 grms. of the pure salt, dissolve in cold water in a beaker, and add dilute sulphuric acid so as to make the solution nearly normal in strength. This may be accomplished by adding to the water solution about one-eighth its bulk of 1 in 5 sulphuric acid. Then run in the permanganate solution until the addition of one drop produces a permanent colour in the liquid. The colour may be detected more easily if the beaker be allowed to stand on a sheet of white paper. The amount of solution used should be such that $\frac{3·92 \times \text{cc. used}}{\text{weight of salt taken}}$ should equal 100, as 3·92 grms. of the salt require 100 cc.

Example (actual):

(*a*) 1·61 grms. of ferrous ammonium sulphate required 41·1 cc. of permanganate solution;

(*b*) 1·506 grms. required 38·4 cc.

$$\frac{3·92 \times 41·1}{1·61} = 100·0$$

$$\frac{3·92 \times 38·4}{1·506} = 100·0$$

The solution was therefore practically deci-normal.

Iodine in the presence of water acts as a gentle oxidising agent similarly to chlorine. For instance SO_2, As_2O_3, H_2S and many other substances can be oxidised a definite stage. On the other hand an iodide like potassium iodide is easily oxidised, or, at any rate, decomposed so that free iodine results. The colour of free iodine is almost a good enough indication by itself, but with starch, an extremely small amount of iodine is made evident. With sodium thiosulphate iodine acts in a very definite manner as far as the iodine is concerned, a perfectly colourless compound being produced.

The two solutions can, therefore, be used as a sort of couple for volumetric work, and are spoken of as "iodine and thiosulphate." They can be employed both in cases of oxidation and reduction, and in consequence have a more extended application than most other volumetric solutions. The above are instances of oxidation, the action with SO_2, or sulphites, being :

$$SO_2 + 2H_2O + I_2 = 2HI + H_2SO_4.$$

Oxidising agents, as chlorine or nitrous acid, liberate iodine from KI and other iodides. Thus :

$$Cl_2 + 2KI = 2KCl + I_2.$$

With sodium thiosulphate the action is :

$$2Na_2SSO_3 + I_2 = 2NaI + Na_2S_4O_6.$$

Chlorine and bromine act much more energetically than this, producing sulphuric acid as one product.

PREPARATION OF A DECI-NORMAL SOLUTION OF IODINE.

$$\frac{I}{10} = 12{\cdot}65 \text{ grms. per litre.}$$

Iodine as purchased is not sufficiently pure for this purpose, and must be purified before being employed. A simple method for purification is to heat ordinary iodine with about one-fourth its weight of potassium iodide on a clock glass,* covered by another accurately fitting glass, the latter of which must not come into contact with the mixture. Pure iodine will then sublime and deposit on the upper glass, any bromine or chlorine which may be present combining with the potassium and liberating an equivalent of iodine. The upper glass is now removed and covered by a third

* Clock glasses can be purchased. They are a little larger than ordinary watch glasses. They can easily be ground flat to fit each other with emery and turps on a piece of ground glass plate.

accurately fitting glass, and when cold, the glasses and iodine are weighed. The combined weight of the containing glasses must be previously known; the difference will then give the weight of iodine. The bulk of solution of $\frac{N}{10}$ strength, which may be made by the iodine present may then be calculated as follows:

Let x = weight of iodine.

Then, since $\frac{N}{10}$ solution contains 12·65 grms. per litre, the required bulk of solution will be $\frac{x \times 1000 \text{ cc.}}{12 \cdot 65}$.

This method of procedure can be generally adopted instead of trying to get a particular weight of any salt, a difficult and slow operation with some substances, and then calculating the proportion of solvent required.

Example:

Weight of glasses + iodine	=	25·7050	grms.
,, glasses only		18·2800	,,
iodine	=	7·4250	,,

$$\text{Bulk of solution required} = \frac{7 \cdot 4250 \times 1000}{12 \cdot 65} = 586 \cdot 9 \text{ cc.}$$

The glasses containing the iodine are now placed quickly in a beaker containing a solution of potassium iodide, nearly twice as much of the iodide as there is iodine by weight. The reason for this is that iodine is scarcely soluble in water alone, but appears to form double iodides—tri-iodides (?) which in the case of the alkaline ones are very soluble.

The solution is now transferred to a convenient measuring flask of less than the required bulk of liquid. The beaker is carefully washed with potassium iodide solution and this water all going into the measuring flask which is finally filled to the mark. The remaining odd cubic centimetres and fractions of water required are run into a large, dry beaker from a burette, the contents of the flask are then poured into this beaker, and the whole well mixed by stirring. The flask should be rinsed out with the mixture, and the rinsings poured back. The solution is then ready for use. It must be kept in a stoppered bottle.

Example.—The above 7·425 grms. of iodine were dissolved in 150 cc. of water containing about 11 grms. of potassium iodide, and the solution transferred to a 500 cc. flask. As the final bulk required was 586·9 cc., 50 cc. were delivered into a dry beaker from a pipette, and the remaining 36·9 from a burette. The whole was then mixed as described.

N.B.—This iodine solution will keep unchanged for a long time in a stoppered bottle if the bottle be wrapped with brown paper to exclude light.

PREPARATION OF A DECI-NORMAL SOLUTION OF SODIUM THIOSULPHATE.

$$\frac{Na_2S_2O_3,5H_2O}{10} = 24{\cdot}8 \text{ grms. per litre.}$$

When iodine reacts with sodium thiosulphate, the equation which represents the reaction is as follows :

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

From this it will be seen that only one half of the sodium reacts with the iodine; hence the weight expressed by $Na_2S_2O_3,5H_2O$ in grms. will be contained in a litre of normal solution, and one-tenth of this amount in a litre of deci-normal.

Pure crystals of thiosulphate are powdered and dried by pressing between the folds of blotting paper; 24·8 grms. are then weighed out accurately, dissolved in water, and the bulk made up to a litre. The solution is mixed in the usual way.

Preparation of starch indicator.—About 60 cc. of water are placed in a large test-tube; as much starch powder as would cover a sixpenny piece is added, and the solution heated and allowed to cool. This indicator should be freshly made each time it is required for a given set of titrations. As is well known, such a starch solution strikes a deep blue colour with iodine, which is destroyed, however, by an excess of sodium thiosulphate. Hence it may be used to determine accurately the end reaction between the two solutions.

TITRATION OF THIOSULPHATE SOLUTION BY IODINE SOLUTION.

25 cc. of thiosulphate solution prepared as above are placed in a beaker; about 75 cc. of water and a little starch solution are added. The iodine solution is then run in from a burette until one drop produces a permanent blue coloration, when the reaction is completed.

Example (actual):

25 cc. of thiosulphate solution required 24·8 cc. of iodine solution.

Check 25 cc. of thiosulphate solution required 24·7 cc. of iodine solution.

The thiosulphate solution was, therefore, too weak, and was brought to standard strength by evaporating until its bulk was reduced to $\frac{247}{250}$ of the original.* It was then found to be correct.

The converse of this titration, *i.e.*, running the thiosulphate solution into the iodine, is conducted by adding the former until the iodine solution has only a faint yellow tinge, then adding the starch indicator, and running in the thiosulphate solution, drop by drop, until the colour is just discharged.

* It is best to evaporate a little too much and again titrate. Standing in an open dish in a dry place will often be sufficient.

PREPARATION OF A STANDARD SOLUTION OF SILVER NITRATE.

The reaction between silver nitrate and soluble chlorides is well known, and, taking sodium chloride, may be represented as follows:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

For most analyses silver nitrate is usually made into a solution of such strength that 1 cc. is the equivalent of 0·001 grm. of chlorine, such solution being found most convenient for the titrations in which the salt is employed. As 108 grms. of silver combine with 35·5 of chlorine, it follows that $\frac{108}{35 \cdot 5} = 3 \cdot 042$ grms. will combine with 1 gr. of chlorine. If therefore a solution be made so that 1 litre contains 3·042 grms. of silver, every cc. would be the equivalent of 0·001 grm. of chlorine. The solution may be prepared by weighing out this quantity of silver and treating with nitric acid; but it is much more convenient in practice to use the prepared salt, 4·788 grms. of which will be found to contain 3·042 grms. of silver.

4·788 grms. of the salt are weighed out accurately and dissolved in water, and the bulk made up to 1 litre. The solution is thoroughly mixed in the usual way, and is then ready for use. It should be standardised by transferring 50 cc. to a beaker by the aid of a pipette, precipitating with HCl, and weighing. The precipitate should weigh 0·2021 grms. (as may be calculated); and the solution should be weakened or strengthened as in the previous cases, according as the precipitate weighs more or less than the above amount.

Silver nitrate may be used for titrations in two ways: 1st, by using potassium chromate as an indicator, in which case the solution must be *neutral;* 2ndly, by observing the point when no further precipitation is caused in the liquid undergoing titration. An example of each of the above methods will be given in illustration.

ESTIMATION OF CHLORINE IN DRINKING WATER.

100 cc. of the sample of water are placed in a beaker, and three or four drops of K_2CrO_4 solution added. The silver nitrate solution is then run in from a burette at the rate of two drops per second, until a distinct red tinge appears in the liquid. A reading is now taken, and another 100 cc. of the water submitted to titration, care being taken, as in the previous estimations, to run in the last few drops carefully, so that the end of the reaction may be exactly determined. Any indefiniteness in the colour may be obviated by adding a little salt solution to the contents of the beaker in which the first rough titration has been performed and stirring, when the red colour will

disappear, and the solution may be used for comparison with the one undergoing the more accurate titration. When one drop of the silver nitrate solution produces a deeper tint than that possessed by the standard, the reaction is completed. Extremely accurate titrations may be made in this manner.

The action of the indicator depends upon the fact that in a solution containing chlorides and a chromate the red silver chromate does not precipitate until the whole of the chlorine present has combined to form silver chloride.

Example:

> 100 cc. of shallow well water required 42·4 cc. of standard silver nitrate solution.
>
> Check 100 cc. required 42·3 cc.

Since 1 cc. of standard silver nitrate = ·001 grm. of chlorine, there was 0·0423 grms. of chlorine present in 100 cc. of solution = 42·3 parts per 100,000. This sample was contaminated by sewage.

Solution of brine and sea-water may be titrated by the above method, and will form useful exercises for the student.

ESTIMATION OF CHLORINE IN COMMON SALT OR SOLUBLE CHLORIDES BY PRECIPITATION METHOD.

Weigh out about 0·08 grms. of the dried specimen, and transfer to a stoppered bottle of about 200 cc. capacity. Dissolve in about 100 cc. of water, and add the silver nitrate solution 1 cc. at a time, placing the stopper in the bottle and shaking well after the addition of each cc. The precipitate of silver chloride formed will by this means settle readily to the bottom of the bottle, leaving the liquid clear. This process is repeated until a given cc. of liquid reagent ceases to produce a cloud in the solution, when the reaction has been completed. A second estimation is now made, running in the whole amount previously used, less 2½ cc., at one operation. The silver nitrate is now added drop by drop, shaking between each drop again being resorted to, until a given drop is seen to produce no precipitate, when the reading of the burette may be taken.

By preparing a standard solution of common salt equal in strength to the silver nitrate solution (an operation the student should now be able to perform), the reverse of the above process may be used, and the amount of silver in a solution estimated by running in the standard salt solution. An excellent exercise for this purpose is to estimate the silver in a silver coin, by dissolving a weighed quantity in nitric acid, and adding the standard salt solution in precisely the same way as the silver nitrate is used in the 'precipi-

tation process. A convenient quantity of the coin to take for the purpose is about 0·1 grm.; or about ·5 grm. of the coin may be dissolved in nitric acid in a beaker, the solution transferred to a 250 cc. flask, and water added to the mark. After mixing, 50 cc. may be withdrawn with a pipette for titration, and the result checked by repeating the process on another 50 cc.

Any doubt as to whether the reagent has been added in excess may be decided by adding the converse reagent drop by drop. The first drop should produce a slight precipitate, the second *nil*. If the end reaction has been considerably exceeded the amount of converse reagent required to react with the excess must be deducted from the amount of solution used.

Example:

> ·5 grms. of a silver-copper alloy were dissolved in about 5 cc. of strong HNO_3, the solution and washings transferred to a measuring flask and diluted to 250 cc.

50 cc. of this solution was transferred by a pipette to a bottle, a little water added, and standard salt solution run in as above described. Since every cc. of solution contained ·001 grm. of chlorine, the silver equivalent of 1 cc. would be $\frac{\cdot 001 \times 108}{35 \cdot 5} = \cdot 003042$ grms. of silver.

1st, 50 cc. required 24·0 cc. of standard salt solution.

2ndly, 50 cc. required 23·8 cc. of standard salt solution.

Since one-fifth of weighed amount was taken, the silver present in total amount taken $= 23 \cdot 8 \times \cdot 003042 \times 5 = \cdot 362$ grms.

Calculating as a percentage $\frac{0 \cdot 362 \times 100}{\cdot 5} = 72 \cdot 4$ per cent. of silver in alloy.

PREPARATION OF A DECI-NORMAL SOLUTION OF POTASSIUM DICHROMATE.

$$\frac{K_2Cr_2O_7}{60} = 4 \cdot 915 \text{ grms. per litre.}$$

When potassium dichromate reacts on a ferrous salt in the presence of an acid, the latter is oxidised to the ferric state, as may be expressed by the following equation:

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O.$$

As in the case of the permanganate solution, the amount of salt required must be calculated from the amount of available oxygen in the salt. The molecule $K_2Cr_2O_7$ contains three available atoms of oxygen; and as oxygen is divalent, a normal solution would be

represented by the weight $\frac{K_2Cr_2O_7}{3 \times 2}$ per litre, and a deci-normal by $\frac{K_2Cr_2O_7}{60}$ = 4·915 *grms.* per litre. The deci-normal solution of this salt is found to be the most convenient strength in practice. To prepare the solution a quantity of potassium dichromate crystals are fused gently in a porcelain crucible, so as to completely expel water. It is removed from the crucible, crushed and powdered, and 4·915 grms. weighed out carefully. The weighed quantity is then dissolved in water in a beaker, the contents and washings poured into a litre flask and water added to the mark. After mixing in the usual way the solution may be standardised as follows:

About 0·2 grm. of clean annealed iron wire (which contains 99·7 per cent. of iron) are placed in a flask of about 150 cc. capacity, and 50 cc. of dilute sulphuric acid poured in from a measuring cylinder. A watch glass of slightly larger diameter than the rim is placed over the flask, which is then warmed until the whole of the metal has dissolved. The solution is immediately poured into a beaker, the flask washed with boiled distilled water and the washings added, and the bichromate solution run in from a burette. The colour of the bichromate turns from yellow to green on entering the liquid, but the end reaction is not visible in the solution. An indicator is found, however, in potassium ferricyanide, which gives a deep blue colour with a ferrous salt, but no such colour with a ferric salt. The ferricyanide, however, must not be introduced into the liquid undergoing titration, but a freshly prepared solution is spotted over the surface of a white tile, and after each addition of bichromate a drop of the liquid is removed by a glass rod and allowed to fall on a spot of ferricyanide. As soon as a given drop of the solution ceases to cause a blue colour in the indicator, the reaction is complete, all the ferrous salt being completely converted into ferric. The last 2 cc. of solution should, as usual, be run in cautiously, drop by drop, and the liquid tested after each addition.

Example :

0·212 grms. of pianoforte wire were dissolved and titrated as above described, and required 37·7 cc. of bichromate solution.

Iron actually present in sample = ·212 × ·997 = ·2113 grm.

$\therefore$ 1 cc. of solution = $\frac{\cdot 2113}{37 \cdot 7}$ = 0·0056 grm. of iron.

The solution was therefore strictly deci-normal.

ESTIMATION OF IRON IN PIG-IRON, STEEL, ETC.

The previous description of the treatment of the iron in standardising the bichromate solution will suffice to show how these estimations may be performed when a standard solution of bichromate is

at hand. The result may be checked by titrating another sample with the $\frac{N}{10}$ potassium permanganate, the preparation of which has been described. It is advisable to heat the acid strongly in dissolving pig-iron, as the carbon present may otherwise form compounds which vitiate the result.

In the case of iron ores, where hydrochloric acid is used to dissolve the compound, the use of permanganate is inadmissible; the bichromate, however, succeeds equally well in this case as when sulphuric acid is employed. When the iron in ferric compounds is to be estimated, the solution must be reduced to the ferrous state by metallic zinc or sulphur dioxide.

It should be remembered that in all titrations in which permanganate or dichromate are employed, the acid present takes a part in the process, and should be present to such an extent as to render the solution about normal (N) in acid strength.

SILICON in iron.—Cast-irons sometimes contain a considerable amount of silicon. When these irons are dissolved in an acid, HCl, some of the silicon becomes oxidised to a hydrate of SiO_2, and in some cases silicon itself may be separated along with graphitic carbon.

Before commencing the analysis of a cast-iron for silicon and carbon, some idea of the approximate amount present is generally to be obtained. Weigh from 2 to 5 grms. of the iron in fine turnings into a beaker, cover with a clock glass and add N HCl in quantities of about 10 cc. at once and at intervals as the action slackens; warm gently. When the action has nearly ceased add 5 cc. $N{\cdot}HNO_3$ and 10 to 20 cc. of $5N{\cdot}H_2SO_4$ and heat on a steam or water bath until nearly all the liquid has evaporated. This will take some time. All the HCl and water will go off, leaving a moderately concentrated sulphuric solution. This will completely dehydrate the silica. Now add about 5 cc. strong HCl, warm gently, and then dilute with hot water. The object is to get all the iron into solution as chloride and sulphate.

Filter off the black residue, which consists of graphitic and amorphous carbon and silica.

Wash thoroughly with hot dilute HCl and then hot water, place the wet, but drained, filter paper in a platinum crucible and ignite for some time in the muffle or over the blowpipe. The residue should be nearly white. If still grey or black some graphitic carbon may still be present. Sometimes this may be burnt off by heating the crucible and blowing in a very gentle stream of oxygen from the oxygen bottle. As a rule, however, the carbon burns off completely after heating for some time in the muffle with a good air draught.

CARBON in cast-iron or steel can also be estimated by burning to CO_2 and absorbing in KHO or in soda-lime, as in the case of organic substances (see p. 272).

Very little apparatus is needed for this analysis. A supply of

oxygen, a combustion-tube about 12 inches long and $\frac{3}{8}$ or $\frac{1}{2}$ in. diameter, a drying and absorbing arrangement, a porcelain boat.

The cast-iron must be in fine turnings or filings. Weigh the porcelain boat, which should be carried in the test-tube carrier, half fill with the iron and weigh again, now cover the iron with as much lead chromate, $PbCrO_4$, as the boat will hold, pressing it down tightly and cleanly on the iron. Arrange the U-tubes as in Fig. 36 (only the KOH, or soda-lime, tube is weighed), insert the boat and allow a gentle stream of oxygen to flow through. Then heat up the tube under the boat, at first with a large Bunsen

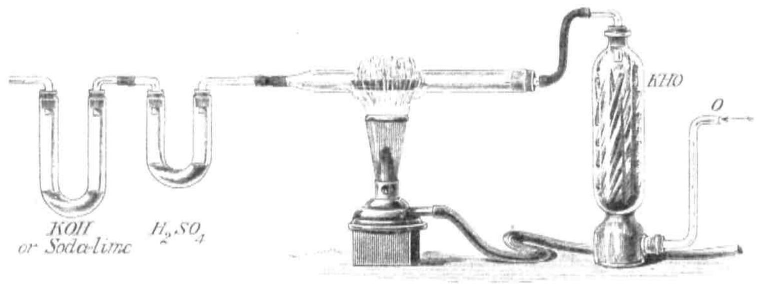

FIG. 36.

flame until the lead chromate melts, and then, if possible, assist with a large blowpipe flame. The iron should glow brightly quite through. The end can be seen pretty distinctly, as when the iron and carbon are fully oxidised the contents of the boat cease to glow or appear any hotter than the glass tube. Allow the oxygen to pass through for at least ten minutes after this. Detach the CO_2 absorption-tube and weigh. Calculate as before; $\frac{3}{11}$ of the gain in weight is C. A boat made from platinum foil will do for many experiments, whereas a porcelain one will only serve once.

Carbon is also present in carbonates, in which case it is generally liberated as CO_2 by an acid as HCl or HNO_3 and absorbed in some alkali.

CO_2 can also be estimated by "loss"—that is, when a carbonate is treated with a weighed quantity of acid, and the CO_2 only is permitted to escape and the remaining salt weighed.

Schrœtter's apparatus is the most elegant for this purpose, but an apparatus to serve the same purpose can most easily be constructed from a small flask or wide mouth weighing bottle, a glass tube with stopper and bulb, and a drawn out test-tube (see Fig. 37).

The small bulb is charged with HNO_3 or HCl, half acid, half water, the drawn out test-tube with small pieces of dry calcium chloride. It should be a rubber stopper. The whole apparatus is weighed, and then 1 to 2 grms. of the carbonate placed in the flask and weighed again. The acid is now allowed to flow very gradually

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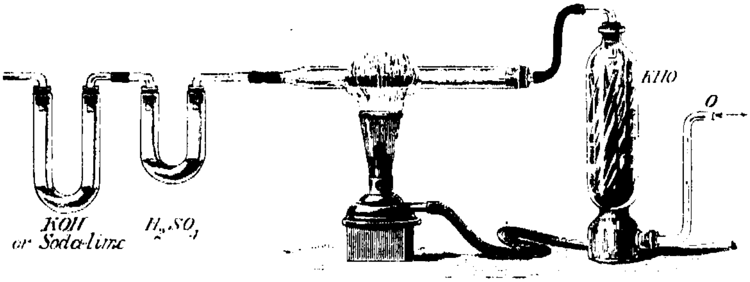

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CO_2 can also be estimated by "loss"—that is, when a carbonate is treated with a weighed quantity of acid, and the CO_2 only is permitted to escape and the remaining salt weighed.

Schrœtter's apparatus is the most elegant for this purpose, but an apparatus to serve the same purpose can most easily be constructed from a small flask or wide mouth weighing bottle, a glass tube with stopper and bulb, and a drawn out test-tube (see Fig. 37).

The small bulb is charged with HNO_3 or HCl, half acid, half water, the drawn out test-tube with small pieces of dry calcium chloride. It should be a rubber stopper. The whole apparatus is weighed, and then 1 to 2 grms. of the carbonate placed in the flask and weighed again. The acid is now allowed to flow very gradually

into the flask; CO_2 is evolved and is dried by the $CaCl_2$ before escaping. Towards the end the flask is gently warmed and a very slow current of (dry) air drawn through for a few minutes only to

FIG. 37.

remove the CO_2 still in the flask and tube. This can be done by attaching a tube at *a* to draw by, and another at *c*, the latter being

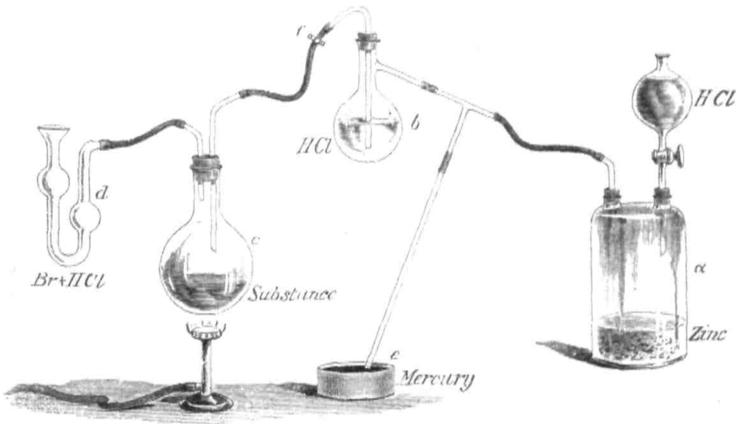


FIG. 38.

connected to a U-tube with $CaCl_2$ or H_2SO_4. The loss of weight at the third weighing = CO_2.

HYDROGEN SULPHIDE is liberated not only when sulphides, as FeS or Sb_2S_3, are dissolved in acids as HCl, but also when

into the **flask**; CO_2 is evolved and is dried by the $CaCl_2$ before escaping. Towards the end the flask is gently warmed and a very slow current of (dry) air drawn through for a few minutes only to

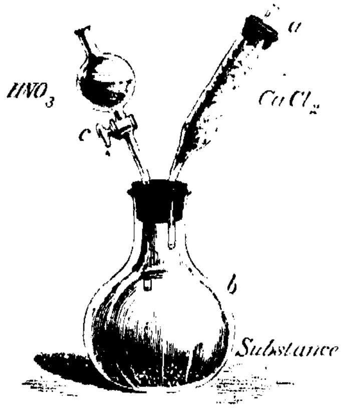


FIG. 37.

remove the CO_2 still in the flask and tube. This can be done by attaching a tube at *a* to draw by, and another at *c*, the latter being

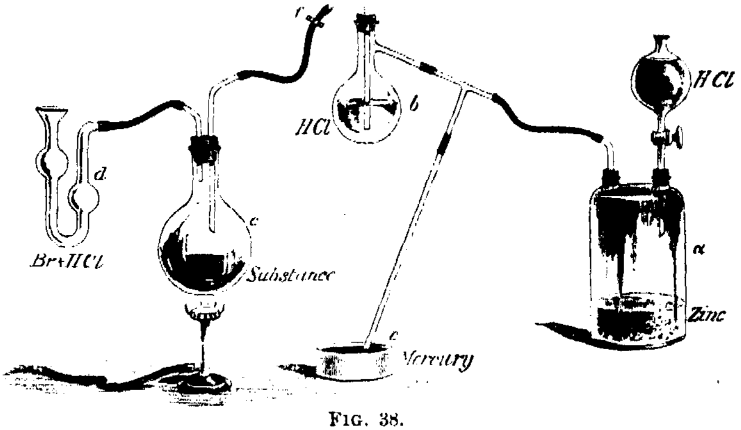


FIG. 38.

connected to a U-tube with $CaCl_2$ or H_2SO_4. The loss of weight at the third weighing = CO_2.

HYDROGEN SULPHIDE is liberated not only when sulphides, as FeS or Sb_2S_3, are dissolved in acids as HCl, but also when

some metals, as iron, &c., which contain sulphur in some form, possibly as dissolved sulphides (?), are acted upon by acids so that hydrogen is generated.

Cast-irons generally contain some sulphur, and when these irons are dissolved in HCl the sulphur escapes with the hydrogen, presumably as SH_2. This gas, on coming in contact with bromine and water or alkaline permanganate solution, is oxidised, the sulphur forming sulphuric acid, which can be converted into barium sulphate.

The amount of sulphur in irons and other metals is generally very small. The apparatus (Fig. 38), in which the metal can be dissolved, and any evolved sulphur compound caught, almost explains itself.

Several grms. of the substance are weighed into *c*, the tube *f* is lifted out of the acid in *b*, and a current of hydrogen sent through the whole apparatus so as to expel air. Then the tube *f* is lowered into the acid in *b*, so that the hydrogen drives some liquid HCl over into the substance-flask, a little at a time, which can be regulated by the screw clip on *f*. The tube *f* slides easily through the cork of the flask. The gas should not pass quicker than two or three bubbles per second through *d*, which contains bromine dissolved in HCl, in which it is more soluble than in water alone. When all the substance is dissolved a gentle heat may be applied to *c*, and the gas thoroughly expelled by the hydrogen current. Any excess pressure of hydrogen is regulated by the escape tube *e*, which dips into half an inch of mercury or a few inches of water.

After the action is complete the contents of *d* are washed out into a beaker and the H_2SO_4 precipitated by $BaCl_2$, and treated as under H_2SO_4, or barium.

Sulphides may sometimes be treated in this manner. If the weighed sulphide, as PbS, be mixed with zinc in the flask *c* the sulphur is more completely and quickly removed as SH_2. Only very small quantities need to be taken for this method.

NITROGEN in nitrates and nitrites, whether mineral or organic, is most easily and quickly estimated by the nitrometer method, which depends essentially on the reduction of HNO_3 or HNO_2 to NO, nitric oxide, by mercury. A nitrate or nitrite of a metal or an organic radicle is decomposed by strong sulphuric acid in contact with mercury, so that the liberated HNO_3 acts at once on the metal.

For instance :

$$2(KNO_3) + H_2SO_4 = K_2SO_4 + 2HNO_3,$$

and the liberated HNO_3 commences to act on the mercury in this sense,

$$8HNO_3 + 3Hg = 3HgN_2O_6 + 4H_2O + N_2O_2,$$

but of course the HgN_2O_6 does not exist for long in the presence of the strong H_2SO_4, but becomes $HgSO_4$ and HNO_3, the liberated nitric commencing another course of decomposition.

The instrument is a graduated tube (*a* in Fig. 39), of about 100 cc. capacity, with a two-holed stopcock. The lower end is joined by stout rubber tube to *c*, which is not graduated and should be quite as wide

as the measuring tube. The measuring tube is filled to the stopper with mercury, which, however, should only stand at about *d* in the tube *b*. The holes in the stopcock should be at least 5 mm. in diameter. The two tubes can be held in any convenient stand, or suspended by a strong cord, the ends fastened to each tube and passing over a bar or hook in a shelf or other support.

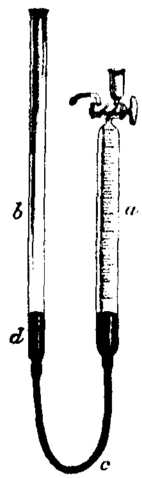


FIG. 39.

To use, fill with mercury, as above, and have the cup at top of *a* dry. Take about ·03 grm. KNO_3 for the first experiment. Introduce the nitrate and then 2 cc. of strong H_2SO_4. Turn the tap quickly so that *nearly all* the acid and the nitrate swimming in it enters the tube; then add another 2 cc. of acid and admit similarly so that it takes the remainder of nitrate with it; repeat the addition of smaller quantities of acid three or four times so as to wash all the nitrate into the tube. This *operation should be done as quickly as possible*, but the *greatest care* must be taken not to let any air in. A little acid must always remain in the cup. Now put a cork loosely in the cup, take *a* from its support and shake briskly, holding by the cup and stopper with one hand and by the point of junction with the rubber tube with the other, by a rapid sideways motion. The acid *must never come as low as the rubber junction*. After shaking an action will be visible and gas will collect. Shake at intervals of five minutes until no more gas bubbles appear and the acid becomes clear.

Measure the length of the acid column on the top of the mercury, which is easiest done by counting the divisions it covers on the tube. Now bring tube *b* close alongside so that the top of the mercury is level with *one-seventh* of the height of the acid column.* Do not handle the gas tube but clamp them both up; hang a thermometer close to and read off the number of cc. of gas after standing for twenty minutes. One litre NO weighs 1·3417 grm. (nearly) ∴ 1 cc. = ·001342 and of this $\frac{7}{15}$ths is nitrogen, since $NO = 14 + 16 = 30$. Barometer and temperature must be read off, but there is no correction for moisture as the H_2SO_4 keeps the gas dry.

A general method of estimating nitrogen, applicable to all kinds of nitrogen compounds (provided they are not very explosive), is to burn in a vacuum tube with copper oxide and catch the nitrogen gas in a measuring tube. A Sprengel mercury pump is indispensable.

If V = observed volume of gas
P = „ pressure
t° = „ temperature
α = Coefficient of expansion = ·00366
V′ = Corrected volume

Then

$$V' = V \frac{P}{760\,(1 + \alpha t^\circ)}.$$

1 cc. NO at NT and P = ·001342 grm. and is equivalent to ·00282 HNO_3, ·000627 N, and ·00452 KNO_3. 1 cc. N at NT and P weighs ·001242.

* Strong sulphuric, being nearly twice as heavy as water, is about one-seventh as heavy as mercury.

The substance is weighed from a bottle on to a piece of copper foil or into a mortar and mixed with CuO in moderately fine powder. This mixture is then introduced into a piece of combustion tube of about 12 inches long, closed at one end. The mortar or piece of copper is washed by small quantities of granular oxide of copper until the tube is three-fourths filled with this granular oxide. This must be well shaken down to the closed end, and then a plug of copper made by *rolling up copper* foil into a cylinder just large enough to enter the tube, inserted. The cylinder should be about 2 inches long.

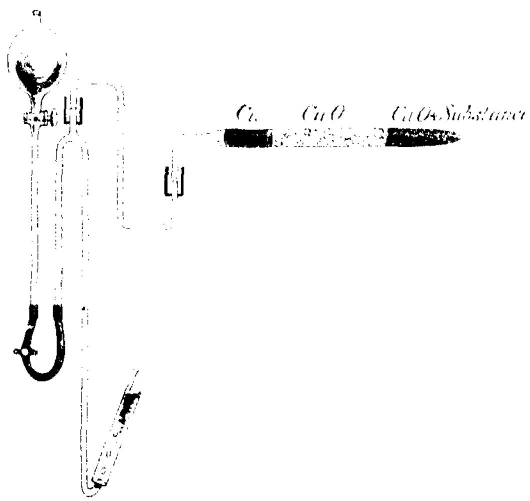


FIG. 40.

The tube is now drawn off so as to fit the Sprengel pump tube. See Fig. 40.

The pump is set in action and the tube evacuated, the portion of the tube containing the copper foil cylinder being at the same time heated to redness. After a complete vacuum is obtained, the gas collecting tube is filled or half filled with strong KHO solution and inverted over the pump end. The pump is stopped and the heat extended backwards to the portion containing the CuO, and when this is red hot to the substance. Water and gases will now come off; when the whole tube has been thoroughly red hot for ten minutes and gases cease to escape into the collecting-tube, the pump is again set in action until a vacuum is obtained.

The tube is now removed by putting a small crucible under the open end and transferred to a tall cylinder full of water. The strong potash solution and any mercury falls out and become replaced by water. The tube is held so that the water inside and out is level and the number of cc. read off, along with temperature and pressure.

As the collected nitrogen is measured over water, the tension of water vapour at the temperature must be deducted from the barometer reading.

Let w = this tension of water vapour. It is = 9·2 mm at 10° C and 12·7 at 15° C.

$V' = \frac{V \times (P - w)}{760 \times (1 + \cdot 00366\, t)}$. As 1 cc. N weighs ·001246, the corrected volume, V′, must be multiplied by this to get the weight of nitrogen.

ELECTROLYSIS.—A number of salts may be decomposed by an electric current and the contained metal deposited in such form that it can be weighed without much difficulty.

One of the easiest examples of this method of quantitative analysis is the decomposition of copper sulphate.

Fig. 41 shows the arrangement. The salt should be weighed in the platinum dish or crucible and dissolved in a small amount

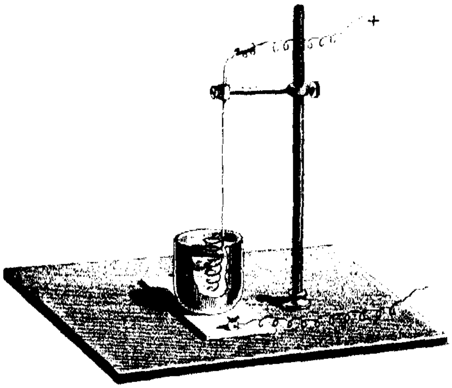


FIG. 41.

of water. The current enters by the spiral of platinum wire, and on the stand is a piece of platinum foil, or sheet copper, to which the return wire is connected. Two or three Bunsen cells, or their equivalent, are quite enough current; in fact, the slower the metal is deposited the *more* coherent it is.

When the solution has become decolorised, test by taking a very small drop, with a rod, on to a plate and adding a drop of potassium ferro-cyanide solution. When no appreciable brown colouration is visible, pour the solution carefully into a white dish to see that no particles of metal are carried away and wash several times, by decantation, with alcohol; dry rapidly in the oven till the alcohol has evaporated and weigh.

If too strong a current be employed the copper is liable to come down in powder and this oxidises very rapidly *during* the *drying*.

Almost any soluble copper or silver salt electrolyses well, but some metals as nickel require an alkali salt, as ammonium or potassium oxalate or sulphate, to be present in order to take up the liberated "ion" SO_4.

APPENDIX II.

REACTIONS OF THE RARE ELEMENTS.

METALS are termed rare either when they occur in nature, as far as is known, to a limited extent and for the most part only in certain minerals and in certain localities, or are not applied technically in any way. Some of the heavy metals, possessing very little affinity for oxygen, such as palladium, rhodium, osmium, ruthenium, and iridium, are found native, and associated with platinum and gold. Others are found in combination with oxygen, such as titanium, uranium, tantalum, and niobium; with sulphur or arsenic, such as tungsten or wolfram, molybdenum, vanadium, thallium, indium, and germanium.

The rare elements usually classified among the so-called light metals, having a specific gravity for the most part of less than 5, and yielding insoluble oxides which are mostly specifically heavier than their metals, such as glucinum, zirconium,* thorium, cerium, lanthanum, didymium, yttrium, erbium, are chiefly met with in nature as oxides in combination with silica (sometimes combined with titanic, niobic, and tantalic acids); and lastly, the metals of the alkali group, whose oxides possess the most pronounced basic character and are soluble in water, such as lithium, rubidium, and caesium, are chiefly met with as salts—carbonates, phosphates, or silicates, sometimes in a soluble condition in sea-water or in mineral springs as chlorides.

As fast as these metals become useful the term rare as applied to them will become defunct, recent research showing that many of these elements are much more widely distributed than was formerly supposed. Yttrium, for instance, according to Sir W. Crookes, seems to be very widely distributed.

It is, of course, not pretended that more than an elementary idea of the treatment of the rare metals or minerals containing them, is here given.

More advanced students should be exercised, when possible, on mixtures containing some of these rare metals as well as the more

* It is high time some systematic nomenclature of these elements was settled upon. "*Zirconium*" is not more "*metallic*" than carbon, and all the members of this group might have a similar ending to their names; as carbon, silicon, zircon, titanon, thoron. Tin would be difficult to alter and retain euphony.

ordinary. They may be worked with the tables given in the text, or better, the student should construct modified tables to suit the altered conditions.

The following is the analytical position assigned to these metals by the various group-reagents:

Group I. *Precipitated by HCl.*—Tungsten, as tungstic acid; niobium, as niobic acid; thallium, as chloride. (Tantalum, as tantalic acid, and molybdenum, as molybdic acid, are soluble in excess of HCl.)

Group II. *Precipitated by SH_2, from a HCl solution, as sulphides:*

(A.) *Insoluble in yellow ammonium sulphide:* palladium, rhodium, osmium, and ruthenium, and thallium in thallic salts.

(B.) *Soluble in yellow ammonium sulphide:* Gold, platinum, iridium, molybdenum, tellurium, selenium, and germanium.

Group III. *Precipitated by NH_4Cl, NH_4OH, and $(NH_4)_2S$:* Uranium, indium (thallium), gallium, as sulphides; glucinum or beryllium, thorium, zirconium, cerium, lanthanum, didymium, yttrium, ytterbium, scandium, erbium, titanium, tantalum, samarium, and niobium, as hydrates. Vanadium, precipitated as sulphide, on adding HCl to the filtrate.

Group IV. None.

Group V. Lithium, caesium, and rubidium.

METALS OF THE ALKALIES.

The alkali metals, caesium, rubidium (potassium, sodium), and lithium are remarkable for their highly electro-positive character, the powerfully alkaline nature of their oxides and hydrates, and the very general solubility of their salts. Caesium appears to be the most highly electro-positive member, whilst lithium shows the least electro-positive character. They exhibit analogous gradations in their respective combining weights, fusion-points, specific gravity, action upon water, and the solubility of their carbonates, thus:

	Caesium.	Rubidium.	Potassium.	Sodium.	Lithium.
Atomic weights	133	85.5	39.1	23	7
Fusion-points.	Below 38·5°	38·5° C.	62·5° C.	96° C.	180° C.
Specific gravity at 15° C.		1·516	·865	·97	·59
Action of the metals upon water.	Decomposes water in the cold, the hydrogen becoming inflamed.	*Do.*	*Do.*	*Do.*, but does not generally inflame the hydrogen.	*Do.*, but with less violence.
Solubility of the respective carbonates.	Cs_2CO_3	Rb_2CO_3	K_2CO_3	Na_2CO_3 Not deliquescent.	Li_2CO_3 Difficultly soluble in water.
	Highly deliquescent, absorbing water speedily from the air. (Cs, Rb, K)				

Lithium, in fact, appears to form the connecting link between the alkali metals and the metals of the alkaline earths.* This is shown more especially by the comparatively insoluble nature of its phosphate and carbonate.

REACTIONS OF THE RARE METALS OF THE ALKALI-GROUP.

1. **CAESIUM**, Cs. Atomic weight, 132·58.—Occurs in very small quantities in many mineral waters, as chloride, and in a few minerals (Lepidolites); in large quantities in the rare felspathic mineral, Pollux, found in Elba, said to contain 34 per cent. of caesium.

Both caesium and rubidium were discovered by Bunsen and Kirchhoff in 1860, whilst examining spectroscopically the saline residue left on evaporating large quantities of the Dürkheim mineral water. The hydrate, CsHO, is very soluble, both in water and alcohol, and very strongly alkaline. The carbonate, Cs_2CO_3, resembles potassium and rubidium carbonate, but is soluble in five parts of boiling alcohol. (Distinction from K_2CO_3, Na_2CO_3, and Rb_2CO_3, which are practically insoluble in alcohol.)

DRY REACTIONS.

When heated on platinum wire, in the inner flame of the blowpipe, volatile caesium salts impart an intense sky-blue colour to the outer flame. (Hence the name of the metal, from caesius, sky-blue.) When examined with a spectroscope, two intensely sky-blue lines, Csα and Csβ, close upon the strontium line, Srδ, are seen (together with various other less distinctly visible lines in the orange, yellow, and green).

REACTIONS IN SOLUTION.

Any salt will give the reactions.

$PtCl_4$ produces a light yellow crystalline (octahedral) precipitate of the double chloride of caesium and platinum, $2CsCl,PtCl_4$, very difficultly soluble in boiling water—·377 part in 100 of water. The corresponding potassium platinic chloride is dissolved by repeated treatment with boiling water.

Tartaric acid produces a colourless transparent crystalline precipitate of hydrogen caesium tartrate, THCs; about eight times more soluble in water than the corresponding rubidium salt.

Method of Separation of Cs from Rb.—$SnCl_4$, added to a solution of the chlorides of Na, K, Li, Rb, and Cs, containing free HCl, forms a heavy white precipitate, consisting of nearly pure caesium stannic chloride, $2CsCl, SnCl_4$. By recrystallisation from a hot hydrochloric acid solution, the crystals are obtained pure. This reaction affords an easy method of detecting caesium in a mixture of the alkaline

* In this connection study the periodic recurrence of the functions of the elements.

chlorides. A hydrochloric solution of $SbCl_3$ acts similarly, by precipitating a crystalline double chloride of $CsCl,SbCl_3$. The precipitate is decomposed by water, but can be washed without decomposition with concentrated HCl. The other alkaline chlorides (K, Na, and Rb) are not precipitated from moderately dilute solutions.

2. **RUBIDIUM**, Rb'. Atomic weight, 85·25.—Occurs widely diffused in nature. It is met with, although only in very small quantities, in a large number of minerals, in Lepidolites and in mineral waters, likewise in the ashes of many plants, such as tobacco, coffee, beetroot, &c.* The metal is obtained, like potassium, by heating the carbonate with carbon. It is white, more easily fusible and convertible into vapour than potassium, and takes fire spontaneously in air. Its oxide rubidia, ORb_2, is a powerful base, and its salts, like the corresponding caesium salts, are isomorphous with those of the metal potassium. The hydrate, RbHO, is strongly alkaline, and very soluble in water and alcohol. The carbonate, Rb_2CO_3, is a deliquescent salt, insoluble in alcohol.

DRY REACTIONS.

Volatile rubidium salts, when heated on a platinum wire in the inner blowpipe flame, colour the outer flame dark red (hence the name rubidium, from *rubidus*, dark red). When examined spectroscopically, two dark red lines, Rbδ, and Rbγ, on the extreme left of the solar spectrum and close to the potassium line, together with two distinctly violet lines, and several weaker lines in the yellow, readily distinguish rubidium compounds.

REACTIONS IN SOLUTION.

Any salt will give the reactions.

$PtCl_4$ produces a light yellow crystalline (octahedral) precipitate of rubidium platinic chloride, $2RbCl,PtCl_4$, very difficultly soluble in boiling water. The solubility of the double chlorides of platinum and potassium, rubidium, or caesium is respectively as 5·18, ·634, and ·377 in 100 parts of boiling water. (Method of separation of K from Rb and Cs.)

Tartaric acid yields a white precipitate of hydrogen rubidium tartrate, THRb, which is soluble in 10·3 parts of water at 25° C.

Rubidium and caesium resemble potassium, also, in forming alums, which differ considerably in their solubility in water.† 100 parts of water at 17° C. dissolve 13·5 parts of potassium alum, 2·27 of rubidium—and only ·62 part of the caesium-alum.

Separation of Caesium from Rubidium.—The platinum salts are first prepared; and after having been gently heated in a current of

* It is just possible that the fertility of some soils for certain species of plants may be influenced by the presence of salts of these metals.

† Recent work shows that rubidium, in its salts, stands between potassium and caesium in general properties; and that all these alkali metal salts are isomorphous.—Tutton, C.S.J.: Alums of Cs.Rb.K.

hydrogen, the CsCl and RbCl can be separated from the metallic platinum by hot water. The two chlorides are next converted into carbonates by digestion with Ag_2CO_3. The solution can then be evaporated to dryness, and the Cs_2CO_3 extracted with boiling alcohol, Rb_2CO_3 being insoluble. Or the carbonates may be converted into acid tartrates, by adding to the solution twice as much tartaric acid as is necessary to neutralise it. The two tartrates are separated by fractional crystallisation, hydrogen rubidium tartrate crystallising out first, being about eight times less soluble in water than the corresponding caesium salt. On ignition, the pure tartrate yields again the carbonate, from which the various salts may then be prepared.

3. **LITHIUM,** Li'. Atomic weight, 7·01.—Appears to be widely diffused in nature, although it is found in quantity only in a few silicates; lithia mica or lepidolite (2 to 5 per cent. of Li), in petalite and spodumene, and in a few phosphates, such as triphylline, or ferrous [manganous] lithium phosphate, $3Fe_3P_2O_8, Li_3PO_4$ (with 3 to 4 per cent. of Li), and amblygonite (6 to 9 per cent. of Li). It has also been found in many mineral springs—most abundantly as yet in a mineral spring in Cornwall—in sea-water, in the ashes of various kinds of tobacco and other plants, and in some meteorites.

The metal lithium is much less oxidisable than potassium and sodium. It makes a lead-grey streak on paper. When freshly cut it has the colour of silver: but it tarnishes quickly on exposure to the air, becoming slightly yellow. It is harder than potassium and sodium, but softer than lead. It floats on rock oil, and is the lightest of all known solids, its specific gravity being only ·59. It decomposes water at the ordinary temperatures, with evolution of hydrogen, forming lithium hydrate, LiHO, but does not melt, and it ignites in air only far above its melting point (180° C.). The oxide, OLi_2, is not deliquescent. The metal is prepared by passing a powerful galvanic current into fused lithium chloride.

DRY REACTIONS.

Lithium salts are more fusible than potassium or sodium salts and impart a very distinct carmine-red colour to a non-luminous flame, when heated on platinum wire. An excess of potassium salt does not materially interfere with the production of this colour; but the presence of a small quantity of soda gives rise to an orange yellow flame. Lithium phosphate requires to be moistened first with hydrochloric acid. Silicates containing lithia must first be decomposed by means of strong sulphuric acid, or by fusion with calcium sulphate, or by treatment with hydrofluoric acid. By means of the spectroscope the occurrence of very minute traces of lithium may be readily detected by a brilliant crimson band, Li*α*, between the lines B and C, and sometimes a faint yellow line, if the flame of a good Bunsen burner be employed.

REACTIONS IN SOLUTION.

Use a solution of lithium chloride, LiCl.

$PtCl_4$ produces no precipitate.

HNa_2PO_4 (hydrogen disodium phosphate)—but not the corresponding potassium salt—produces on boiling a white precipitate of lithium phosphate, $2Li_3PO_4 + OH_2$, very little soluble in cold water (250 parts), soluble in HCl, and reprecipitated only, on boiling, after neutralisation with NH_4OH.

Lithium carbonate, especially after having been fused, is difficultly soluble in cold water, hence alkaline carbonates yield from concentrated solutions of lithium salts a crystalline precipitate of lithium carbonate, Li_2CO_3 (1 part of the carbonate requires 100 parts of cold water for its solution, but less of boiling water). It is insoluble in alcohol. When fused for a short time on platinum the metal shows signs of corrosion, after washing.

Hydrogen lithium tartrate is soluble in water.

Lithium silicofluoride is almost insoluble.

Separation of Lithium.—From potassium, as well as caesium and rubidium, it may be separated by means of $PtCl_4$. From sodium, by converting the two alkalies into the chlorides, evaporating to dryness, and treating the dried chlorides in a stoppered bottle with a mixture of ether and absolute alcohol. In the course of a few days the LiCl will be found dissolved out, NaCl (like KCl) being insoluble in absolute alcohol and ether.

Extraction of Lithium from Triphylline or Lepidolite.—Dissolve the powdered mineral in HCl, with a little HNO_3 (in order to convert Fe'' into Fe^{iv}), neutralise with NH_4OH, when $Fe_2P_2O_8$ and $Mn_3P_2O_8$ are precipitated. The solution, on filtering, may contain some more phosphoric acid, which may be removed by adding BaS, and filtering off the precipitated $HBaPO_4$. On removing the excess of BaS, with a few drops of H_2SO_4, and evaporating the filtrate, and driving off the ammonium salts by gentle ignition, lithium chloride is left. The hydrate may be prepared from this by evaporation with sulphuric acid to obtain Li_2SO_4, and the addition of $Ba(HO)_2$, and filtering. The excess $Ba(HO)_2$ is next cautiously removed from the filtrate by means of H_2SO_4. On evaporation, white crystalline, strongly alkaline lithium hydrate, LiHO, is left.

REACTIONS OF THE RARE METALS OF GROUP III.

Group III. comprises the Rare Metals, Uranium, Indium (Thallium), Glucinum, Thorium, Zirconium, Cerium, Lanthanum, Didymium, Titanium, Tantalum, Niobium, Yttrium, Erbium, Terbium, Samarium, and Vanadium.

As it is extremely difficult to obtain the salts of these metals in a pure state commercially, and as the price charged for them puts them out of the reach of most students, it will be preferable to sketch out briefly how some of their minerals can be made to furnish the several salts.

(A.) Rare metals precipitated by the group-reagents, ammonium chloride, hydrate and sulphide, in the form of oxides (hydrates).

Besides the metals aluminium and chromium, already treated of in the main portion of the book, there are:

1. **BERYLLIUM** (Glucinum), Be″. Atomic weight, 9·2.—This metal occurs only in a few minerals as a silicate, in phenacite, Be_2SiO_4, combined with aluminium silicate; in beryl, $Be_3Al_2Si_6O_{18}$, and in smaragdite, in euclase, and some other rare metals, such as leucophane.

The metal is obtained, like the metal aluminium, from its chloride. It is white and has a specific gravity of 2·1. It resembles zinc and aluminium in dissolving in HCl, as well as KHO, with evolution of hydrogen. Its oxide is a white powder, insoluble in water. It may be prepared by fusing the finely powdered native silicate with four times its weight of fusion-mixture, decomposing the mass with HCl and evaporating to dryness to separate the SiO_2. From the HCl filtrate both the Al_2O_3 and BeO are precipitated by means of ammonia. On boiling the precipitate, however, for some time with ammonium chloride, NH_3 is evolved, and beryllium is dissolved out as chloride, $BeCl_2$. The insoluble $Al_2(HO)_6$ remains behind. The pure gelatinous hydrate, $Be(HO)_2$, can then be precipitated from the filtrate by means of ammonium hydrate. On ignition it yields the white anhydrous oxide, BeO of specific gravity 3·08.

From the oxide the salts may be obtained by dissolving in the respective acids. Glucina (beryllia) combines both with acids and bases. Its salts are colourless, and of a sweet, slightly astringent taste; they show an acid reaction.

DRY REACTIONS.

Beryllium compounds give no characteristic reactions in the dry way. BeO and $Co(NO_3)_2$ yields a grey mass when heated on charcoal.

REACTIONS IN SOLUTION.

Use a solution of beryllium sulphate, $BeSO_4$.

The group-reagents, NH_4HO and $(NH_4)_2S$, as well as the fixed caustic alkalies and alkaline earthy bases, precipitate beryllium hydrate, $Be(HO)_2$ (flocculent), soluble, like $Al_2(HO)_6$, in excess of the fixed alkalies, but not in ammonia. On boiling, $Be(HO)_2$ is almost completely reprecipitated from a dilute NaHO or KHO solution. (Distinction from Al_2O_3.) Like Al_2O_3, it is reprecipitated also on the addition of ammonium chloride.

$(NH_4)_2CO_3$ gives a white precipitate of basic beryllium carbonate, freely soluble in excess, reprecipitated as basic carbonate on boiling. (Distinction from Al_2O_3.)

Na_2CO_3 or K_2CO_3 precipitates likewise white carbonate, soluble only in large excess of the precipitants.

$BaCO_3$ precipitates beryllium completely, even in the cold.

Besides these characteristic reactions, may be mentioned the

difficultly soluble double sulphate, $K_2SO_4,BeSO_4 + 30H_2$, which the readily soluble beryllium sulphate forms, when mixed with potassium sulphate solution.

Separation of Al_2O_3 from BeO.—Dissolve in HCl; pour slowly, and with continued stirring, into a warm concentrated solution of $(NH_4)_2CO_3$. A precipitate forms, consisting of $Al_2(HO)_6$, the solution containing the beryllium as double carbonate. Neutralise filtrate with HCl; boil and add NH_4OH. $Be(HO)_2$ is precipitated.

The exact position of beryllium is not quite settled. It has many analogies with Al and also with Mg and Zn. Its specific heat indicates that the atomic weight 13·6 is correct, and that its oxide is Be_2O_3. The characters of some salts point to its being a dyad of atomic weight 9·03, and the oxide as BeO or GlO. It was first termed glucinum, from the sweet taste of the salts, and then beryllium, from its occurrence in the beryl.

2. **ZIRCONIUM,** Zr^{iv}. Atomic weight, 89·37.—Found as silicate, chiefly in the rare mineral zircon, $ZrSiO_4$. This silicate is not attacked by acids, and the finely divided substance must be decomposed by fusion at a high temperature, with fusion mixture, or better with KHO. The mass is extracted with water, evaporated to dryness with HCl, in order to remove SiO_2, and to decompose the insoluble sandy-looking disodium zirconate, $ZrNa_2O_3$, and is then precipitated with ammonia. The element itself has been obtained in white metallic-looking scales, of specific gravity 4·1, by the decomposition of the double fluoride of potassium and zirconium, $2KF,ZrF_4$, by means of metallic aluminium. The element is also obtained mixed with MgO, on heating ZrO_2 with magnesium powder. The hydrate is a voluminous white body, resembling $Al_2(HO)_6$. It dries up to yellowish, transparent lumps, $Zr(HO)_4$, which dissolve readily in acids. On ignition this hydrate loses its water, and also undergoes a molecular change, when the dioxide, ZrO_2, is no longer soluble in dilute acids.

Zirconic salts, obtained by dissolving the hydrate in dilute acids, are colourless, and of an astringent taste.

DRY REACTIONS.

Of all the earthy oxides, ZrO_2 is the only one which remains entirely unaltered when admitted to the action of the oxy-hydrogen blowpipe. It gives out a very intense and pure light. Moistened with $Co(NO_3)_2$, and intensely heated, the mass becomes of a dirty violet colour. With borax, ZrO_2 yields a colourless glass which becomes slightly opaque when cold.

REACTIONS IN SOLUTION.

Use a solution of the sulphate, $Zr(SO_4)_2$, or chloride.

The group-reagents, $(NH_4)_2S$ or NH_4OH, produce a white flocculent precipitate of the hydrate, $Zr(HO)_4$, insoluble in excess; insoluble also in NaHO or KHO (distinction from Al and Be.)

KHO or NaHO, same precipitate, insoluble in excess, not

dissolved by a boiling solution of NH_4Cl (distinction from Be).

$(NH_4)_2CO_3$ produces a white flocculent precipitate of a basic carbonate, readily soluble in excess, reprecipitated on boiling (*distinction from* Al).

K_2CO_3 and Na_2CO_3, same precipitate, redissolves in a large excess of K_2CO_3, especially of $KHCO_3$ (distinction from Al).

$BaCO_3$ gives no precipitate in the cold, and precipitates zirconium salts imperfectly, even on boiling.

Oxalic acid gives a bulky precipitate of zirconium oxalate (distinction from Al and Be), insoluble in excess, difficultly soluble in HCl, soluble in excess of ammonium oxalate (distinction from Th).

HF produces no precipitate (distinction from Th and Y).

$Na_2S_2O_3$ precipitates zirconium thiosulphate, ZrS_2O_3 (distinction from Y, Er, and Di). The separation takes place on boiling, even in *the presence of 100 parts of water to one of* ZrO_2 (distinction from Ce and La).

Zirconium sulphate, $Zn(SO_4)_2$, forms with potassium sulphate an insoluble double sulphate of Zr and K, insoluble in excess of K_2SO_4 (distinction from Al and Be). When precipitated cold, it dissolves readily in a large proportion of HCl, but is almost insoluble in water and HCl, when the K_2SO_4 is added to a hot solution (distinction from Th and Ce).

Turmeric paper, when dipped into a hydrochloric acid solution of a zirconium salt, acquires a brownish-red colour after drying in the water-bath (distinction from Th). But titanic acid—the only other metal which affects turmeric paper under the same circumstances—colours the paper brown, and its presence may therefore prevent the zirconium from being recognised. If the TiO_2 be, however, first reduced by means of zinc and HCl, to the state of sesquichloride—the reduction being marked in the solution by a change of colour to pale violet or blue—it no longer colours turmeric paper, and any change in the colour of the latter is then due to zirconium alone. The reaction requires great care, however, as, on exposure of the paper to air, the Ti_2O_3, passing again to the state of TiO_2, would in its turn colour the turmeric paper, and thus render the observation doubtful.

It was at one time thought that the jargon, a variety of zircon, contained a new earthy metal provisionally termed jargonium.

The oxide, ZrO_2, has recently been used as a substitute for CaO, in the oxyhydrogen light and in other gas lights, on account of its greater durability and incandescent power.

This element will doubtless before long become useful in the formation of bronzes and other alloys.

3. **THORIUM,** Th^{iv}. Atomic weight, 231·96.—Found in a few rare minerals only—viz., in thorite (orangite), consisting principally of a hydrated silicate, $ThSiO_4,2OH_2$, in monachite, pyrochlor and monazite.

Thorite is decomposed by moderately concentrated H_2SO_4, and

also by concentrated HCl. The oxide or anhydride, ThO_2, is white when cold, yellow when hot. The moist hydrate dissolves readily in acids; the dried hydrate only with difficulty. Thorium salts containing colourless acids are white.

DRY REACTIONS.

ThO_2, when heated before the blowpipe, remains infusible; it imparts no tinge to the flame, and gives a colourless borax bead. It yields no characteristic reaction with $Co(NO_3)_2$.

REACTIONS IN SOLUTION.

Thorium sulphate, $Th(SO_4)_2$, may be used.

$(NH_4)_2S$ or NH_4OH (group-reagents), precipitates the white gelatinous hydrate, $Th(HO)_4$, *insoluble in excess.*

KHO or NaHO, same precipitate, insoluble in excess (distinction *from Al and Be*).

Ammonium potassium and sodium carbonates precipitate white *basic thorium carbonate, readily soluble in excess of the precipitants*, difficultly soluble in dilute solutions (distinction *from Al*). *From a solution in $(NH_4)_2CO_3$ thorium carbonate* is reprecipitated, even at 50° C.

$BaCO_3$ *precipitates thorium salts completely in the cold.*

Oxalic acid produces a white precipitate (distinction from Al and Be), not *soluble in excess nor in dilute mineral acids;* soluble in ammonium acetate, containing free acetic acid (*distinction from Y and Ce*).

HF precipitates gelatinous thorium tetrafluoride, ThF_4, which becomes pulverulent after some time; the precipitate is insoluble in water and in HF (distinction from Al, Be, Zr, and TiO_2).

$Na_2S_2O_3$ precipitates thorium thiosulphate, $Th(S_2O_3)_2$, mixed with sulphur, from neutral or acid solutions. The precipitation is not complete (distinction from Y, Er, and Di).

A boiling concentrated solution of K_2SO_4 precipitates slowly, but completely, the whole of the thorium sulphate as white crystalline insoluble potassio-thorium sulphate, $K_4Th(SO_4)_4 + 2OH_2$ (distinction from Al and Be), soluble with difficulty in cold, and also in hot water, readily on the addition of some HCl.

The oxide ThO_2 is the main constituent of the incandescent gas mantles.

4. **YTTRIUM,** Y‴. Atomic weight, 89·6; and 5, **ERBIUM,** Er‴. Atomic weight, 166.—These very rare elements are only found in a few minerals, in ytterbite, or gadolinite, orthite, yttrotantalite, &c. The metals have never been obtained pure. Yttrium and erbium, and possibly terbium, occur together in nature, and closely resemble the metals of the cerite group. They differ from most other earths in being completely soluble in acids, even after ignition, and from the cerite oxides, by not forming an insoluble double sulphate with potassium sulphate. In other respects they exhibit almost the same behaviour with reagents, and can only be

approximately separated from each other. The colour of the yttrium salts is white. Erbium salts have a more or less bright rose tint, crystallise readily, and possess a sweet astringent taste. Anhydrous YCl_3 is not volatile (distinction from Al, Be, and Zr).

$(NH_4)_2S$ or NH_4OH (group-reagents) precipitate the hydrates, insoluble in excess. Large excess of $(NH_4)_2S$ somewhat prevents the precipitation of yttrium hydrate.

KHO or NaHO precipitates white hydrates, $Y(HO)_3$ or $Er(HO)_3$, insoluble in excess (distinction from Al and Be). The precipitation of yttrium by alkaline hydrates is not prevented by the presence of $T(HO)_2$ (distinction from Al, Be, Th, and Zr), yttrium being slowly but completely precipitated as tartrate. Erbium is not completely precipitated.

K_2CO_3 and Na_2CO_3 precipitate white carbonates, difficultly soluble in excess, more readily soluble in $KHCO_3$ and in NH_4HCO_3 (but not so readily as $BeCO_3$). On boiling the whole of the yttria is deposited (distinction of Y from Al, Be, Th, Ce, and Di). NH_4Cl decomposes $Y_2(CO_3)_3$, with evolution of NH_3 and CO_2, and formation of YCl_3. Saturated solutions of $Y_2(CO_3)_3$ in $(NH_4)_2CO_3$ or Na_2CO_3 have a tendency to deposit a double carbonate.

$BaCO_3$ produces with erbium salts no precipitate, either in the cold or on heating; and yttrium salts are but imperfectly precipitated on heating (distinction of Er and Y from Al, Be, Th, Ce, La, Di).

Oxalic acid produces a precipitate of white yttrium oxalate, $Y_2(C_2O_4)_3 + 6OH_2$ (distinction of Y from Al and Be), insoluble in excess, difficultly soluble in dilute HCl and partially dissolved by boiling with ammonium oxalate. Erbium salts are likewise precipitated as oxalate, $Er_2(C_2O_4)_3 + 6OH_2$, in the form of a light rose-coloured, heavy sandy powder.

HF precipitates white amorphous hydrated yttrium fluoride, insoluble in water and HF; soluble, before ignition, in mineral acids; decomposed only by strong H_2SO_4. (Distinction of Y from Al, Be, Zr, and Ti.)

A cold saturated solution of $Y_2(SO_4)_3$ becomes turbid between 30°–40° C., and on boiling is precipitated almost entirely.

$Er_2(SO_4)_3$ forms with K_2SO_4 potassio-erbium sulphate,

$$Er_2(SO_4)_3,K_2SO_4,$$

difficultly soluble in cold water, when hydrated, but readily soluble in the anhydrous condition, and on warming.

Potassium yttrium sulphate dissolves readily in water and in a solution of K_2SO_4. (Distinction of Y and Er and Sm from Th, Zr, and the metals of the cerite group.)

When erbium nitrate is heated on a platinum wire in a gas flame, it imparts an intense greenish colour to the flame, which, when seen through the spectroscope, shows bright lines in the

yellow and green, also in the orange and in the blue in an otherwise continuous spectrum. These bright lines coincide with certain black so-called absorption bands, which erbium gives when white light is passed through a concentrated solution of its salts. These absorption bands are characteristic for erbium, as yttrium solutions show none under like circumstances.

In a "radiant matter tube" yttrium compounds give a phosphorescence, the spectrum of which exhibits a number of lines, the most striking of which are in the yellow or orange. Although only present in small amount in any known mineral, Sir W Crookes' experiments show that yttria is exceedingly widely distributed in nature.

Separation of Y from Er.—The different solubility of the nitrates of erbium and yttrium in water has been made available for the separation of these two closely allied metals. On heating a mixture of their nitrates to incipient decomposition, and dissolving the residue in boiling water, the solution deposits on cooling rose-red crystals of basic erbium nitrate, whilst the mother-liquor contains chiefly yttrium nitrate. By repeating the same process of separation many times, the earths may be obtained approximately pure by finally igniting the nitrates.

Thulium and holmium are other supposed elements in this group. Their characters have not yet been made out with sufficient clearness as not to be doubtful.

The only reliable method of separation is to fractionally precipitate and examine each fraction with the spectroscope, or place in a vacuum tube through which an induction charge can be sent, and the phosphorescent glow, given by many substances, examined by the spectroscope.

6. **YTTERBIUM**, Yb‴. Atomic weight, 172·6.—Euxenite is the most abundant source of this earth, where it is accompanied by the oxides of six or seven closely related elements, scandium, thulium, samarium, &c. Ytterbia has been separated by the very tedious process of evaporating the nitrates and heating considerably, whereby basic salts insoluble in water are formed, Sc, Th, Di, Er, Y, being relatively less soluble than ytterbium. The operations have to be repeated many times. The pure earth is obtained from the nitrate by addition of oxalic acid and igniting the oxalate formed.

Yb_2O_3 is a heavy white infusible powder, easily soluble in warm dilute acids. The solutions are colourless. Specific gravity of oxide = 9·175. Its salts have a sweet taste. The nitrate is scarcely decomposed by heating, and remains soluble (characteristic).

NH_4OH precipitates the hydrate $Yb(HO)_3$. The sulphate, $Yb_2(SO_4)_3$, is soluble in water. The acid selenite, $Yb_2(SeO_3)_3$, H_2SeO_3,$4OH_2$, is precipitated from neutral solutions, and is white and insoluble. The oxalate, $Yb_2(C_2O_4)_3$,$10OH_2$, is insoluble in dilute acids.

• 7. **SCANDIUM**, Sc‴. Atomic weight, 43·98.—This earth concentrates in the insoluble basic nitrates on the separation of Yb.

Its nitrate is next to Yb in difficulty of decomposition by heat, the two earths differing greatly in this respect from Er, Tb, Yt, &c. Yb and Sc may be separated by heating their nitrates, or by precipitation of scandium potassium sulphate by addition of K_2SO_4. $Sc_2(SO_4)_3,3K_2SO_4$ is quite insoluble, the Yb salt soluble. Sc_2O_3 is white, specific gravity 3·864, and resembles MgO or BeO; it is infusible, and not very soluble in acids.

NH_4OH precipitates $Sc(HO)_3$, insoluble in excess of KHO or ammonia. The oxalate is slightly soluble in water, 1 in 1080. Other salts are very similar to those of Yb.

A number of rare minerals, as euxenite, samarskite, orangite, &c. &c., contain many of these elements.

CERIUM, Ce^{ii}, ^{iii}, and ^{iv}. Atomic weight, 140·42. **LANTHANUM**, La‴. Atomic weight, 138·53. **DIDYMIUM**, Di‴, or ^{v}. Atomic weight, 144·57. These three rare metals, with, possibly, samarium, constitute, like Yt, Er, Yb, Sc, and Tb, a group which may conveniently be studied together. The most abundant of the few cerium minerals is cerite, a hydrated silicate of the three metals Ce, La, and Di, as well as of iron and calcium. The finely powdered mineral is readily and completely decomposed by boiling with concentrated HCl or aqua regia; or by fusion with fusion-mixture; or, lastly, by boiling with concentrated H_2SO_4.*

CERIUM. Specific gravity = 6·72. This metal exists both in the dyad, pseudo-triad, and tetrad condition. Thus it forms the several oxides:

CeO (?)	Ce_2O_3	$Ce^{iv}O_2$	and Ce_3O_4 or CeO,Ce_2O_3 (?)†
Cerous oxide	Ceric oxide (sesquioxide)	Ceric dioxide	Ceroso-ceric oxide, or triceric tetroxide

Ceric oxide and ceric dioxide are both capable of combining with acids to form two series of salts. They are colourless, or slightly amethyst-red, and acid to litmus. Cerous chloride is not volatile (distinction from Al, Be, and Zr). Cerous sulphate is not entirely soluble in boiling water.

DRY REACTIONS.

All cerium compounds give with borax, or microcosmic salt, in the outer flame, a clear bead, which is dark red while hot (distinction from the preceding earths), fainter or nearly colourless on cooling. In the inner flame, a colourless bead, or, if ceric oxide is present, a yellow opaque bead, is obtained. Lanthanum compounds give

* The student is strongly advised to refer to the method of separation of samarium from cerium, didymium, lanthanum, &c. &c., devised by Sir W. Crookes, F.R.S., *Roy. Soc. Trans.* 1885, and later. The methods here mentioned appear very crude and imperfect in comparison with the patiently carried out processes there described.

† The existence of CeO is somewhat doubtful.

colourless beads, and didymium compounds give with borax colourless, or, if in large quantity, pale rose-coloured beads, in both flames, and with microcosmic salt, in the reducing flame an amethyst-red bead, inclining to violet.

REACTIONS IN SOLUTION.

A. **CEROUS COMPOUNDS.**—A solution of cerous chloride Ce_2Cl_6, may be used.

Ammonium sulphide (group-reagent) throws down the white cerous hydrate, $Ce_2(HO)_6$, insoluble in excess.

Ammonium hydrate precipitates a basic salt, insoluble in excess: the presence of tartaric acid prevents the precipitation by NH_4OH (distinction from Y), but not by KHO.

KHO or NaHO precipitates white cerous hydrate, insoluble in excess, which turns yellow on exposure to the air, or when acted upon by oxidising agents, such as chlorine water, sodium hypochlorite, &c., being converted into yellow hydrated ceroso-ceric oxide, $Ce_3O_4,3OH_2$ (distinction from Al and Be).

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$, produces a white precipitate of cerous carbonate, $Ce_2(CO_3)_3$, sparingly soluble in excess of the fixed carbonates, somewhat more soluble in $(NH_4)_2CO_3$; insoluble in water and CO_2; decomposed by dilute acids.

$BaCO_3$ precipitates cerium salts slowly, but completely, on standing.

Oxalic acid, or ammonium oxalate, precipitates cerium compounds completely, even from moderately acid solutions, as a curdy white precipitate (turning slowly crystalline) of cerous oxalate, $Ce_2(C_2O_4)_3,9OH_2$, insoluble in excess of the precipitants (distinction from Zr), but soluble in a large excess of HCl. On ignition cerous oxalate leaves yellowish-white ceroso-ceric oxide, Ce_3O_4, or CeO_2 (distinction from Al and Be, which form soluble oxalates).

A *saturated solution of potassium sulphate* produces a white crystalline precipitate of potassio-cerous sulphate, $3K_2SO_4,Ce_2(SO_4)_3$; even from somewhat acid solutions (distinction from Al and Be); difficultly soluble in cold water, readily soluble on heating, quite insoluble in a saturated solution of K_2SO_4 (distinction from Y and Er); soluble in much dilute HCl. With dilute solutions the precipitates take some time to form.

This characteristic precipitate, as well as the easily distinguishable oxalate, and the yellow precipitate of ceroso-ceric oxide—free from La and Di, precipitable in the filtrate as oxalates—which oxidising agents produce, serve to distinguish cerium from all other metals.

Separation of Ce from La and Di.—A convenient method of oxidising and separating cerous salts consists according to Gibbs, in treating the mixed oxides with PbO_2 and dilute HNO_3 analogous

to the oxidation of manganous to a higher oxide), when the solution turns yellow, even if only small quantities of cerium be present. By evaporating the yellowish solution to dryness and heating sufficiently to drive off part of the HNO_3, so as to form a basic cerium nitrate, insoluble *in water or dilute* HNO_3, lanthanum and didymium can be dissolved out as nitrates. After removing the lead nitrate from the solution by SH_2, the La and Di (containing also *samarium*) are *precipitated as oxalates. The residuary basic cerium* nitrate is dissolved in fuming HNO_3, any lead removed by SH_2, and the cerium precipitated as oxalate.

B. **CERIC COMPOUNDS.**—Salts of CeO_2, such as the sulphate, oxalate, &c., are yellow, and are either difficultly soluble or insoluble in water. *Dyad (triad) (?) cerium appears, in fact, to give* rise to more stable compounds; thus, CeO_2, when heated with HCl, does not form $CeCl_4$, but yields $(CeCl_2) + Cl_2$.

Oxidising agents, such as Cl, passed into a solution of KHO, containing $Ce_2(HO)_6$ in suspension, sodium hypochlorite, PbO_2, HNO_3, HgO, or potassium permanganate, convert cerous into ceric compounds, and furnish methods for the separation of Ce from La and Di. Reducing agents produce the reverse chemical action. Cerium resembles in this respect iron rather than aluminium.

LANTHANUM, Specific gravity = 6·163.—This metal forms only proto-salts, which are colourless when free from didymium salts, and possess a sweet astringent taste. Lanthanum oxide is white, and is not altered, even by strong ignition (distinction from Ce), being still readily soluble in acids. Both the oxide and the hydrate turn red litmus-paper blue. It decomposes ammonium salts, in solution, on boiling, with evolution of NH_3. Lanthanum resembles in this respect magnesium. A solution saturated in the cold of lanthanum sulphate deposits a portion of the salt already at 30° C. (distinction from Ce). In its reactions lanthanum closely resembles cerium.

REACTIONS IN SOLUTION.

Use a solution of lanthanum chloride, $LaCl_3$.

Ammonium sulphide and hydrate precipitate basic salts, which pass milky through the filter on washing.

KHO or NaHO, precipitates lanthanum hydrate, $La(HO)_3$, insoluble in excess, unalterable in the air, or in the presence of oxidising agents (distinction from Ce).

Ammonium carbonate gives a precipitate which is insoluble in an excess of the precipitant (distinction from Ce).

K_2CO_3, Na_2CO_3, $BaCO_3$, oxalic acid or potassium sulphate, give similar precipitates as with cerium salts.

When the slimy precipitate which a cold dilute solution of lanthanum oxide yields, on supersaturation with ammonia, is washed repeatedly with cold water, and a few small crystals of iodine added

to it, a blue coloration is produced, which gradually pervades the entire mixture (characteristic for La compounds only).

DIDYMIUM, Specific gravity = 6·544.—The metal forms likewise only proto-salts, coloured a pure pink, as the sulphate, or rose-red, *sometimes a faint violet, as the nitrate.* The *oxide is soluble in acids* after strong ignition. The peroxide Di_2O_3, has been prepared by heating $Di(NO_3)_2$ in a stream of oxygen. In contact with water Di_2O_3 is slowly converted into the hydrate, without acquiring an alkaline reaction. It rapidly attracts CO_2, and is readily dissolved by the weakest acids. It expels ammonia from ammonium salts when boiled with them. The chloride, $DiCl_2$, is not volatile. The nitrate, on heating, is converted into a basic salt (distinction from La), which is grey when hot and also when cold (distinction from Er). A saturated solution of didymium sulphate begins to deposite red crystals of the salt at 38° C., until at 100° C. one part of the salt only is held in solution by 50 parts of water (method of separation of La from Di). Didymium salts resemble in their chemical deportment lanthanum and cerium salts.

REACTIONS IN SOLUTION.

Employ a solution of the chloride, $DiCl_2$, or sulphate, $Di_2(SO_4)_3$.

Ammonium sulphide and hydrate (group-reagents), precipitate basic salt, *insoluble in* NH_4OH, *but slightly soluble in* NH_4Cl, with displacement of NH_3.

KHO, or NaHO, precipitate gelatinous didymium hydrate, $Di(HO)_3$, resembling $Al_2(HO)_6$, but of a pale rose colour, it is insoluble in excess, and does not alter in the air.

Alkaline carbonates produce a copious precipitate of didymium carbonate, $Di_2(CO_3)_3$, insoluble in excess of the precipitants (distinction from Ce), but slightly soluble in a concentrated solution of NH_4Cl.

$BaCO_3$ precipitates didymium compounds slowly (more slowly than Ce or La), and *never completely*.

Oxalic acid precipitates didymium salts, $Di_2(C_2O_4)_3$, almost completely; ammonium oxalate completely. The precipitate is difficultly soluble in cold HCl, but dissolves on heating.

A concentrated solution of K_2SO_4, or better still, Na_2SO_4, precipitates didymium solutions more slowly and less completely than cerous solutions, as a rose-white potassio-didymium sulphate, $Di_2(SO_4)_3,K_2SO_4 + OH_2$, slightly soluble in water, less soluble in an excess of the reagent, difficultly soluble in hot HCl.

When a ray of white light is sent through a didymium solution, and examined by the spectroscope, dark bands are seen in the continuous spectrum. Dilute solutions show these absorption bands in the yellow and green; concentrated solutions exhibit, in addition, several other well-defined narrower bands in various other parts of the spectrum.

Several chemists have separated, by more or less tedious methods,

the earth didymia into what appears to be either several modifications or actually different substances.

The reactions above given must be understood as being on the "rough" didymia.

TERBIUM, Tb. Atomic weight, 148·5.—The oxide, Tb_2O_3, of this metal has been separated from Yt, Er, and Nb in North Carolina samarskite by converting the oxides of Yt, Er, and Tb into formates, and submitting them to fractional crystallisation. The oxide is a dark yellow powder, which becomes white when ignited in hydrogen. Its salts are isomorphous with those of white Yt, Di, and Er.*

TITANIUM, Ti'' and ^{iv}. Atomic weight, 50·25.—This, as well as the two next following metals (usually treated of in Group III., because they are precipitated by the group-reagents, chloride, sulphide and hydrate of ammonia), differ entirely from the previously treated metals. Their anhydrides, $Ti^{iv}O_2$, $Ta^{v}{}_2O_5$, and $Nb^{v}{}_2O_5$, are analogous to SiO_2, Sb_2O_5, &c., and are found in nature either in the uncombined state (TiO_2), or combined with various metallic bases, as titanates, tantalates, and niobates. The metal titanium has a great affinity for N, with which it combines directly.†

Titanium is found as anhydride (almost pure) in the minerals rutile, anatase, and brookite; combined with bases, chiefly lime, in titanite, $CaTiSiO_5$, in titaniferous iron, and in small quantities in many iron ores, in fire-clays, and generally in silicates. (Hence its occurrence in blast-furnace slags, as cyano-nitride, $TiCy_2,3Ti_3N_2$, in bright copper-coloured cubes.)

Titanium forms several oxides, of which two are known with certainty, and one whose existence is probable, viz.:

TiO	Ti_2O_3	TiO_2
Titanous oxide (probable).	Titanic oxide (sesquioxide).	Titanic anhydride.

The last oxide, acting as a weak base, and forming mostly very unstable salts, and likewise as an acid, is the only one which is of sufficient importance to be studied analytically.

In order to prepare some pure titanic anhydride, finely powdered rutile is fused with 3 parts of K_2CO_3, the fused mass powdered and treated with cold water, which removes SiO_2 and alkaline silicates, and leaves insoluble potassium titanate, K_2TiO_3, together with ferric oxide. This is washed by decantation or on a filter, with cold water, and dissolved in cold dilute HCl. On diluting considerably with water and heating to boiling, for some time, the whole of the titanium is precipitated as meta-titanic hydrate, H_2TiO_3 (Fe being held in

* For details on Methods of separation of these metals, the student is advised to see Crookes' "Select Methods," chap. iii.

† Probably most metals are capable of forming N compounds or nitrides. Heating the metal with NH_3 is the best known method at present of forming these compounds. A considerable number of these compounds are known (see Nitrogen).

solution by the acid), which differs from (ortho-) titanic acid in being quite insoluble in all acids, except strong sulphuric acid, whilst titanic hydrate (obtained by precipitation with alkalies), of exactly the same composition, is readily soluble even in dilute H_2SO_4 or HCl. The precipitated meta-titanic acid is usually tinged yellow, owing to some ferric oxide which is carried down with it. It is best, therefore, to filter off, to wash with a solution of ammonium chloride, and redissolve the precipitate in strong H_2SO_4. After dilution with water, it is reprecipitated once more by long-continued boiling, and is then all but free from iron. (Method of separation from Al, Be, Y, and Th.) A more expeditious method for separating the iron oxide consists in precipitating the two metals from the dilute acid solution by means of ammonium sulphide, as FeS and H_4TiO_3, and to treat the precipitate with aqueous sulphurous acid, which dissolves the FeS, and leaves the pure ortho-titanic acid.

Another method consists in fusing the titanium compound with six times its weight of $KHSO_4$, till it yields a clear mass; dissolve in a large quantity of cold water, acidulate with dilute H_2SO_4, when meta-titanic acid is precipitated as above. SiO_2, if present, is not attacked by $KHSO_4$, and remains in the insoluble residue.

Pure TiO_2 may also be obtained by fusion with acid potassium fluoride, and dissolving the fused mass in dilute HCl. Potassium titanic fluoride, K_2TiF_6, which is difficultly soluble in water (1 part requires 96 parts at 14° C.), is collected on a filter and washed with cold water, and purified by recrystallisation from boiling water. Its aqueous solution, when precipitated with ammonia, yields titanic hydrate, which on ignition is converted with incandescence into pure titanic anhydride—white, when only feebly ignited, yellowish or *brownish, when intensely ignited.*

SiO_2, or silicates, containing traces of TiO_2, may be decomposed with HF. H_2SO_4 must likewise be added in order to prevent a portion of the titanium from being volatilised with the SiF_4.

DRY REACTIONS.

Titanium compounds, when heated on charcoal before the blowpipe, are not reduced to the metallic state (distinction from In). Heated in a borax bead *(on charcoal), or better still,* **in a bead of microcosmic salt, pure TiO_2, or a titanite, containing bases which do not themselves colour the borax bead, yields in the outer flame a colourless glass, but in the inner flame, a glass which is yellow while hot, but assumes a violet colour on cooling. The reduction is promoted by the addition of a little zinc or tin. If** *some* **$FeSO_4$ be added, the bead obtained in the inner flame becomes blood-red.**

REACTIONS IN SOLUTION.

Use a solution of titanic acid in HCl.

Alkaline hydrates and sulphides and carbonates, as well as $BaCO_3$, produce a bulky white precipitate of (ortho-) titanic

hydrate, H_2TiO_3, which is insoluble in an excess of the precipitants. When thrown down in the cold, and washed with cold water, it is readily soluble in dilute HCl, or in dilute H_2SO_4. Washing with hot water converts it into insoluble meta-titanic hydrate. The presence of TH_2 prevents the precipitation. (Iron, as well as Ni, Co, Zn, and U, which are precipitated by ammonium sulphide in the presence of tartaric acid and ammonium hydrate (the metal Mn is not), may thus be separated from TiO_2.)

K_4FeCy_6 produces a dark-brown precipitate.

Infusion of galls, brownish precipitate, which speedily turns orange-red.

HNa_2PO_4 throws down the titanic acid almost completely from an acid solution as a white gelatinous phosphate, which when washed and dried leaves a basic salt, probably $HTiPO_5,H_2O$.

Metallic tin or zinc, immersed in a HCl solution of TiO_2, evolves hydrogen, and reduces the TiO_2 to Ti_2O_3, which gives rise to a pale violet or blue coloration, and finally throws down a dark-violet precipitate, which is rapidly oxidised to white TiO_2, with decomposition of the water or when exposed to the air. This reaction frequently reveals the presence of TiO_2 in the analysis of iron ores, during the process of reduction with zinc, previous to the estimation of the iron by potassium permanganate.

TANTALUM, Ta^v. Atomic weight, 182. **NIOBIUM,** Nb^v. Atomic weight, 93·7.—This group of metals occurs only in a few minerals, found in a few localities, and then only in small quantities. The difficulty of detecting mere traces of them may account for their having been overlooked in others in which they have since been found, viz., in tinstone and wolfram.

In some of the minerals, either tantalum or niobium prevails, such as in tantalite and in niobite (columbite).

Tantalum and niobium exist chiefly in the pentad condition, as is evidenced by the composition of their oxides (anhydrides), chlorides, fluorides, &c. &c., viz.:

Tantalic anhydride, Ta_2O_5.	Chloride, $TaCl_5$.	Fluoride, TaF_5.
Niobic „ Nb_2O_5.	„ $NbCl_5$.	„ NbF_5.

A lower oxide, $Ta^{iv}_2O_4$, and sulphide, $Ta^{iv}_2S_4$, are said to exist. In tantalates and niobates, the acids closely resemble arsenic or phosphoric acid; they can exist as meta- $HTa(Nb)O_3$, pyro- $H_4Ta(Nb)O_7$ or ortho- $H_3Ta(Nb)O_4$, tantalic (niobic) acids.

TANTALIC and **NIOBIC ANHYDRIDES** are prepared from tantalites or niobites, by fusing the finely powdered mineral with three parts of $HKSO_4$. The fused mass is extracted with water, whereby the bases are principally removed as sulphates. The residuary Ta_2O_5 and Nb_2O_5 are washed and fused once more with hydrogen potassium sulphate, &c. The residue after having been

well washed is dissolved in HF, and a boiling solution of HF,KF gradually added to it. The liquid, on cooling or on concentration, yields difficultly soluble potassium fluo-tantalate, $2KF,TaF_5$ (soluble in about 150–200 parts of water only), whilst the mother-liquors contain potassium fluo-oxyniobate, $2KF,NbOF_3,OH_2$, which is soluble in 12·4 to 13 parts of water (distinction also from titanium, which forms $2KF,TiF_4$, soluble in 96 parts of water). These two salts may be purified by recrystallisation; and on decomposing them by heating with H_2SO_4, tantalic and niobic sulphates and potassium sulphate are left; this latter can be boiled out with water. When H_2SO_4 is expelled from the insoluble tantalic or niobic sulphate by strong ignition, or by heating in an atmosphere of ammonium carbonate, Ta_2O_5 or Nb_2O_5 is left.

TANTALUM.—The anhydride is a white powder. When strongly ignited it turns a pale yellow, without emitting any light, and becomes insoluble in HCl or strong H_2SO_4 (distinction from TiO_2).

Fused with KHO it is rendered soluble in water; fused with NaHO, it forms chiefly sodium meta-tantalate, $NaTaO_3$, insoluble in excess of NaHO, but soluble in water. When a solution of soda is added to this solution, sodium tantalate is precipitated. Hydrated tantalic acid dissolves in HF from a concentrated solution of which KF precipitates fine needle-shaped crystals of potassium fluo-tantalate. By prolonged boiling with water, this soluble salt changes to an insoluble compound, $Ta_2O_5(2KF,TaF_5)$, or $K_4Ta_4O_5F_{14}$, the formation of which affords the means of detecting the smallest quantity of fluo-tantalate in mother-liquors containing potassium fluo-oxyniobate.

DRY REACTIONS.

Microcosmic salt dissolves Ta_2O_5 to a colourless bead in both flames, and does not acquire a blood-red tint by the addition of ferrous sulphate (distinction from TiO_2).

REACTIONS IN SOLUTIONS.

Use a solution of $KTaO_3$ in water.

The tantalates of the alkali metals are soluble in water, all others (formed by double decomposition) are insoluble in water and decomposed by acids.

HCl precipitates Ta_2O_5, at first, then redissolves it in excess.

CO_2 passed through a solution of an alkaline tantalate, precipitates acid, or anhydro-tantalate.

Ammonium hydrate or sulphide precipitates from a HCl solution tantalic hydrate, or an acid ammonium tantalate; $\overline{T}(HO)_2$ prevents the precipitation.

Ammonium chloride or sulphate precipitates tantalic hydrate $HTaO_3$.

K_4FeCy_6 gives from acidified solutions a yellowish-white precipi-

(uranium yellow) is used as a pigment in glass and porcelain manufactures.

DRY REACTIONS.

Borax and microcosmic salt give with uranium compounds in the inner flame of the blowpipe, green beads, in the outer flame yellow beads, which acquire a yellowish-green tint on cooling. The oxides of uranium are not reduced by fusion with Na_2CO_3 on charcoal.

REACTIONS IN SOLUTION.

A. **URANOUS COMPOUNDS**.—Use a solution of uranous sulphate, $U(SO_4)_2$. Prepared by dissolving uranoso-uranic oxide in hot oil of vitriol, diluting with water and evaporating *in vacuo*.

Uranous salts constitute powerful reducing agents. They are green, or greenish-white, and yield green aqueous solutions.

$(NH_4)_2S$ forms a black precipitate of uranous sulphide, US.

Alkalies throw down red-brown gelatinous uranous hydrate, $U(HO)_4$.

Alkaline carbonates precipitate green uranous hydrate, soluble in excess, especially in excess of ammonium carbonate.

Uranous salts become oxidised to uranic salts, by exposure to air, or by treatment with nitric acid, &c. Gold and silver salts are speedily reduced by them, and ferric salts are reduced to ferrous salts.

B. **URANIC COMPOUNDS**.—Use a solution of uranylic nitrate, $UO_2(NO_3)_2$.

Uranic salts are yellow, they are mostly soluble in water, and are reduced to uranous salts by SH_2 and by alcohol, or ether and in sunlight.

$(NH_4)_2S$ produces in the cold a chocolate-brown precipitate of uranylic sulphide, containing also ammonium sulphide and water. It is insoluble in yellow ammonium sulphide. On warming or boiling the liquid which contains the uranylic sulphide, $(UO_2)S$, suspended in it, the precipitate splits up into sulphur and the black oxide, UO, which is insoluble in excess of the sulphide. Uranylic sulphide dissolves readily in neutral ammonium carbonate. [Method of separation of U from Zn, Mn, and Fe.]

Alkaline hydrates produce a yellow precipitate, consisting of acid uranate of the alkali metal; insoluble in excess of the precipitant: not precipitated in the presence of tartaric acid.

The ammonium precipitate is soluble in a solution of ammonium carbonate, and ammonium sulphide does not precipitate the uranium from this solution.

Alkaline carbonates give a light yellow precipitate, consisting (in the case of potassium carbonate) of potassio-uranic carbo-

nate; readily soluble in an excess of the precipitant. By treating the liquid with dilute sulphuric acid, as long as effervescence takes place, an acid uranate is precipitated. [Method of separation of U from Al and Fe^{iv}.]

$BaCO_3$ completely precipitates a solution of a uranic salt, even in the cold. [Separation of U from Ni″, Co″, Mn″, Fe″ and Zn.]

K_4FeCy_6 produces a reddish-brown precipitate. (Most delicate special reaction.)

$K_6Fe_2Cy_{12}$ produces no change.

Metallic zinc does not precipitate metallic uranium from its solutions.

THALLIUM, Tl′ and ‴. Atomic weight, 203·7.—This metal was discovered by Crookes in 1861. It occurs in many kinds of copper and iron pyrites, but invariably in very minute quantities; also in many kinds of crude sulphur, in some of the deposits from the flues leading from the pyrites furnaces to the lead chambers of sulphuric acid works, and in the deposits in the chambers themselves. It has, moreover, been found in lepidolite, in preparations of cadmium and bismuth, in ores of zinc, mercury, and antimony, in the ashes of some plants, and in some saline waters, &c. &c.

The metal is most economically extracted from thalliferous flue-dust. The dust is stirred up with boiling water, the insoluble portion allowed to settle, and the clear supernatant liquid syphoned off. On the addition of concentrated hydrochloric acid, impure thallious chloride, TlCl, is precipitated. This impure chloride is dissolved in concentrated sulphuric acid, evaporated till the hydrochloric acid, as well as the greater portion of the sulphuric acid, has been driven off, then dissolved in boiling water, and a rapid current of sulphuretted hydrogen passed through the solution, whereby all the metals of the SH_2 group are precipitated. On now introducing plates of zinc into the dilute acid filtrate, spongy metallic thallium is precipitated, which can be readily removed from the zinc, and obtained in lumps or bars by pressure. *It must be preserved under water.*

It is softer than lead and of the same colour, of specific gravity 11·8. It melts at 290° C., and may be distilled in hydrogen. The metal and all its salts are highly poisonous.

The salts may be prepared by dissolving the metal in the respective acids, or by the double decomposition of soluble thallium salts.

Thallium forms two series of compounds: thallious and thallic. In the thallious the metal exists as a monad, and in the thallic as a triad. Thus we have:

Thallious oxide .	OTl_2	Thallic oxide .	Tl'''_2O_3
Thallious chloride .	TlCl	Thallic chloride .	$Tl'''Cl_3$, &c.,

together with several intermediate compounds.

In some of its chemical relations thallium differs from all other metals. In many respects it resembles the alkali metals, as, for instance, in forming the readily soluble and highly alkaline thallious oxide and carbonate, an insoluble double platinum salt, an alum analogous to ordinary potash alum, and a series of thallious phosphates analogous to the alkaline phosphates. In most other respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting point, specific heat, and electric conductivity.

DRY REACTIONS.

Thallium compounds impart an intense green colour to the blowpipe flame. The spectrum of thallium shows one very striking emerald-green line, *Tlα*, and hence its name from *θαλλός*, green.

REACTIONS IN SOLUTION.

A. **THALLIOUS COMPOUNDS.**—Employ a solution of thallious sulphate, Tl_2SO_4, or nitrate, $TlNO_3$.

Thallious salts are for the most part colourless and soluble in water, such as the nitrate, sulphate, phosphate, tartrate, and acetate. Some are difficultly soluble, *e.g.*, the carbonate and chloride, and a few are almost insoluble, *e.g.*, the iodide. They react neutral to test-paper, and possess a slight metallic taste. Thallious oxide, OTl_2, is colourless and fusible; it dissolves in water, the solution is colourless, alkaline, caustic, and absorbs carbonic anhydride from the air. It also dissolves in alcohol.

Thallious salts are difficultly converted into thallic salts; powerful oxidising agents, such as nitric acid, are without effect on them. They require boiling and evaporating with aqua regia to convert them into the higher salts.

SH_2 does not precipitate strongly acidified thallious solutions unless As_2O_3 be present, when a part of the thallium is carried down with the arsenious sulphide, as a brownish-red precipitate. Neutral or very slightly acidified solutions are incompletely precipitated by SH_2. From acetic acid solutions the whole of the thallium is thrown down as black thallious sulphide, STl_2.

$(NH_4)_2S$ (group-reagent) precipitates the whole of the thallium as thallious sulphide, insoluble in ammonia, alkaline sulphides, or potassium cyanide. Readily soluble in dilute hydrochloric, sulphuric, or nitric acids, but difficulty soluble in acetic acid. When exposed to air, thallious sulphide is rapidly converted into thallious sulphate. On heating, it fuses and volatilises.

Alkaline hydrates do not precipitate aqueous solutions of thallious salts.

Carbonated alkalies produce a precipitate only from concentrated solutions, Tl_2CO_3 being soluble in 20 parts of water.

HCl or a soluble chloride throws down white thallious chloride TlCl; the precipitate subsides readily, and is unalterable in the air. It is very slightly soluble in boiling water, and still less so in hydrochloric acid.

KI precipitates, even from the most dilute thallious solutions, light yellow thallious iodide, TlI, which is almost entirely insoluble in water, but somewhat more soluble in a solution of potassium iodide. This constitutes the most delicate reaction for thallious salts.

K_2CrO_4 precipitates yellow thallious chromate, Tl_2CrO_4, insoluble in cold nitric or sulphuric acid.

$PtCl_4$ precipitates difficultly soluble, pale orange-coloured thallious platinic chloride, $2TlCl,PtCl_4$.

Zinc precipitates metallic thallium.

B. **THALLIC COMPOUNDS.**—Employ a solution of thallic chloride, $TlCl_3$.

Thallic salts are easily distinguished from thallious salts by their behaviour with caustic and carbonated alkalies, which precipitate brown gelatinous thallic hydrate, TlOHO, insoluble in excess.

Thallic oxide is scarcely acted on by concentrated sulphuric acid in the cold; on heating, thallic sulphate, $Tl_2(SO_4)_3,7OH_2$, is obtained. When a solution of thallic sulphate is boiled, oxygen is given off, and a thallious salt left. When treated with HCl, thallic oxide yields the chloride $TlCl_3$ as a white crystalline mass, which on heating splits up into TlCl and Cl_2.

HCl or a soluble chloride produces no precipitate.

SH_2 reduces thallic to thallious salts, with precipitation of sulphur.

$H_2C_2O_4$ produces a white pulverulent precipitate of oxalate.

HNa_2PO_4 gives a white gelatinous precipitate.

H_3AsO_4 or a soluble arsenate gives a yellow gelatinous precipitate.

K_2CrO_4 does not precipitate thallic salts.

KI gives a precipitate of TlI and I_2.

INDIUM, In^{iv}, and pseudo-triad. Atomic weight, 113·4.—Has hitherto only been found as a rare and insignificant constituent of some zinc ores (zinc-blende from Freiberg), in the metallic zinc prepared from these ores, and in tungsten.

Indium is a white, highly lustrous metal resembling platinum, soft and ductile, of specific gravity 7·42. It fuses easily at 176° C. It is not oxidised in the air or in water. Dilute HCl or H_2SO_4 dissolves it readily, hydrogen being given off. Concentrated sulphuric acid dissolves it with evolution of SO_2. It is readily soluble also in cold dilute nitric acid. The oxide, In'''_2O_3, is brown when hot, straw-coloured when cold, and is readily reduced when heated on charcoal, or in a current of hydrogen gas. A black dioxide, $In^{iv}O_2$, exists likewise.

The principal salts of indium, viz., the sulphate, $In_2(SO_4)_3,9OH_2$, the nitrate, $In(NO_3)_3$, and the chloride, $InCl_3$, are freely soluble in water. The chloride is volatile and hygroscopic.

DRY REACTIONS.

Indium and its compounds impart to the flame a peculiar bluish tinge. When examined with the aid of a spectroscope two characteristic blue lines can be seen, a bright one in the blue, and a feebler one in the violet. They are, however, very transient. The sulphide gives more persistent lines than the chloride.

REACTIONS IN SOLUTION.

A solution of any of the above salts may be used.

SH_2 *produces no precipitate in the presence of a strong acid.* Indium is, however, precipitated like the metal zinc, from slightly acid solutions, or in the presence of acetic acid. The slimy precipitate of indium sulphide, In_2S_3, is of a fine yellow colour.

$(NH_4)_2S$ produces at first a white precipitate from a solution, containing ammonium tartrate, said to consist of In_2S_3 and hydrogen. It turns yellow on the addition of acetic acid. The sulphide is insoluble in cold, but soluble in the hot sulphide, and on cooling it separates again of a white colour.

Alkaline hydrates produce a white bulky precipitate of indium hydrate, $In(HO)_3$, resembling aluminium hydrate, quite insoluble in alkalies. The presence of tartaric acid prevents the precipitation.

Alkaline carbonates precipitate white gelatinous carbonate. When recently precipitated it is soluble in ammonium carbonate, but not in the fixed alkaline carbonates. On boiling, indium carbonate separates again.

$BaCO_3$ precipitates indium salts in the cold as basic salts. (Distinction from Zn, Mn, Co, Ni, and Fe.)

HNa_2PO_4 throws down a bulky white precipitate.

Alkaline oxalates produce a crystalline precipitate.

Zinc precipitates the metal in the form of white shining laminæ.

VANADIUM, V‴ and v. Atomic weight, 51·3; specific gravity = 5·5.—Only obtained as a grey powder. It oxidises in the air, but resists most acids and alkalies. Occurs only in a few rare minerals, principally in vanadite, or lead vanadate and oxychloride, $Pb_5V_3ClO_{12}$, analogous in composition to pyromorphite, also to a very small extent in many iron ores (clay and pea iron ores), and as Roscoe discovered, in the copper bearing beds at Alderley Edge, and Mottram St. Andrew's, Cheshire.

Vanadite or mottramite, $(PbCu)_3(VO_4)_2$, may be made the starting-point for preparing the several vanadium compounds. The mineral

is dissolved in nitric acid, and the lead and arsenic precipitated by SH_2, which at the same time reduces the vanadic pentoxide, V_2O_5, to tetroxide, V_2O_4. The blue filtered solution is then evaporated to dryness, and the residue digested in ammonia, when the vanadic tetroxide becomes reoxidised into pentoxide. The ammonium vanadate can be precipitated as a white powder from this solution by introducing a lump of sal-ammoniac, being scarcely soluble in a saturated solution of this salt. By exposure to a temperature below redness in an open crucible, ammonia is expelled and V_2O_5 is left.

Vanadium forms several oxides, oxychlorides, chlorides, sulphides, which show that the metal is closely allied to the phosphorus and arsenic group. Thus:

Oxides.	Oxychlorides.	Chlorides.	Sulphides.
V_2O	—	—	—
V_2O_2	—	VCl_2	—
V_2O_3 (black)	—	VCl_3	—
V_2O_4 (blue)	—	VCl_4	V_2S_4
V_2O_5	$VOCl_3$	—	V_2S_5

The most important of these compounds is the pentoxide, or vanadic anhydride, analogous in composition with phosphoric, arsenic, antimonic, tantalic, and niobic anhydrides. It combines in different proportions with bases, forming, like the other anhydrides referred to, three series of salts, viz., ortho-, pyro-, and meta-vanadates. Fused with Na_2CO_3, it yields sodium ortho-vanadate, Na_3VO_4; but when boiled with a solution of an alkali, it forms the meta-vanadate, the latter class of vanadates being more stable than the ortho-salts. Alkaline vanadates are soluble in water, inversely to the quantity of free alkali or alkaline salt present. Hence they are precipitated from their solutions by excess of alkali, or by salts as NH_4Cl. (Most characteristic reaction.)

Vanadic anhydride has a reddish-yellow colour, and is difficultly soluble in water (1000 parts), forming a light yellow solution which reddens litmus paper. It dissolves also in the stronger acids to red or yellow solutions, which become frequently decolorised by mere boiling. It unites, however, with bases more readily than with acids.

A sulphuric acid solution of the acid when considerably diluted with water, and treated with zinc or sodium amalgam and warmed gently, turns first blue, then green, and finally from lavender to violet. The V_2O_5 becomes reduced to V_2O_2; and on the addition of ammonium hydrate, a brown precipitate of the hydrate of the dioxide (hypovanadious acid) forms, which absorbs oxygen more rapidly than any other known reducing agent, and bleaches organic colouring matter (indigo-solution, &c.) as quickly as chlorine.

Many organic substances, such as oxalic or tartaric acid, sugar, alcohol, reduce vanadic acid, especially in the presence of strong mineral acids, to the blue V_2O_4. The same takes place when SO_2 or SH_2 is added to its solutions in acid.

DRY REACTIONS.

Borax dissolves V_2O_5 to a clear bead, colourless, or, with large quantities of the anhydride, yellow, in the outer flame, beautiful green in the inner flame. With larger quantities of vanadic acid it looks brownish whilst hot, and only turns green on cooling.

REACTIONS IN SOLUTION.

Use a solution of sodium metavanadate, $NaVO_3$.

Orthovanadates are generally yellow or reddish-yellow, both in the liquid and solid state. By boiling in water, the orthovanadates of the alkalies are converted into colourless metavanadates. On the addition of an acid to a solution of neutral or orthovanadate, the solution becomes yellowish-red, owing to the formation of anhydro-salts.

Ammonium, barium, and lead metavanadates are but sparingly soluble in water. The alkaline vanadates are more soluble in pure water than in water containing free alkali or a salt: hence they are precipitated in the presence of the latter. All are soluble in nitric acid, but insoluble in alcohol.

$(NH_4)_2S$ (group-reagent) produces a brown coloration in the liquid, and on acidulating with HCl, or better with H_2SO_4, the soluble ammonium sulphovanadate is decomposed, and brown pentasulphide, V_2S_5, mixed with sulphur, is precipitated; the liquid at the same time generally acquires a blue colour. It dissolves with red-brown colour in aqueous solutions of alkaline carbonates, hydrates, and sulphhydrates.

If an acidified solution of an alkaline vanadate be shaken up with ether containing peroxide of hydrogen, the aqueous fluid acquires a red-brown colour, like that of ferric acetate, whilst the ether remains colourless. This reaction is extremely delicate.

Vanadic and chromic acids are the only acids whose salts give rise to red-coloured solutions. They are, however, differently affected by reducing agents.

Many of the elements which are so difficult to reduce to a metallic state, such as uranium, vanadium, tungsten, titanium and some of the cerium metals have been found to reduce and melt in the electric furnace. They take up carbon, in varying amounts, however, and in some cases form definite carbides after the manner of calcium.

REACTIONS OF THE RARE METALS OF GROUP II.

Group II. comprises the rare metals, precipitated as sulphides by SH_2, from a hydrochloric acid solution, viz.:

(A) *As sulphides, insoluble in yellow ammonium sulphide:* Palladium, rhodium, osmium, ruthenium.

1. **PALLADIUM,** Pd'' and iv. Atomic weight, 106·2.—Occurs native in platinum ores, principally, however, alloyed with gold and silver, in a gold ore found in Brazil. The gold dust is fused together with silver, and the granular alloy heated with nitric acid, in which silver and palladium only dissolve. On the addition of sodium chloride, silver is removed as chloride, and the palladium may then be precipitated as palladious cyanide by means of mercuric cyanide, and the $PdCy_2$ decomposed by ignition.

The metal greatly resembles platinum, but is somewhat darker in colour. Its specific gravity is 11·8. Of all the so-called platinum metals it fuses most readily, not in an ordinary Bunsen burner, but easily in the oxy-hydrogen flame. Palladium is sparingly soluble in pure nitric acid, but dissolves more readily in the red acid. It dissolves slightly in boiling concentrated sulphuric acid, and is readily attacked by fusing with hydrogen potassium sulphate. The best solvent for it, as for most other platinum metals, is aqua regia. The metal oxidises when heated in air, the surface becoming coloured from films of oxide. It absorbs hydrogen to a large extent, and if heated over a spirit lamp or gas flame will even decompose the hydrocarbon vapours, carbon being deposited on the metal. Palladium forms several oxides and chlorides, in which the metal exists either as a dyad or tetrad, thus:

Palladium suboxide	. Pd_2O			$PdCl$ (?)
Palladious oxide .	. PdO	Chlorides	.	$PdCl_2$
Palladic „ .	. PdO_2	„	.	$PdCl_4$

PALLADIOUS SALTS.

The oxide PdO is obtained on gently igniting palladious nitrate. It is black, and its hydrate dark-brown. Both part with their oxygen upon ignition, leaving spongy palladium. The nitrate may be prepared from the metal by dissolving in nitric acid and concentration over a water-bath. It forms then a brownish-red non-crystallisable mass.

Palladious salts are mostly soluble in water; they are brown or reddish-brown; their dilute solutions are yellow.

REACTIONS IN SOLUTION.

A solution of palladious nitrate, $Pd(NO_3)_2$, is used.

OH_2 precipitates a brown basic salt from solutions containing slight excess of acid only.

SH_2, or $(NH_4)_2S$, throws down from acid or neutral solutions black palladious sulphide, PdS, insoluble in alkaline

sulphide, but soluble in boiling hydrochloric acid, and readily soluble in aqua regia.

KHO, or NaHO, precipitates a yellowish-brown basic salt soluble in excess.

Soluble carbonates precipitate brown palladious hydrate, $(Pd(HO)_2$, soluble in excess, reprecipitated on boiling.

Ammonium hydrate or carbonate produce no precipitate from the nitrate, but decolorise the dark-brown solution, forming double palladammonium salts.*

HI, or soluble iodides, give, even in very dilute solutions, a black precipitate of palladious iodide, PdI_2, somewhat soluble in excess of KI. (Most characteristic reaction for Pd.) It serves for the detection of iodine in the presence of chlorine and bromine.

$HgCy_2$ gives a yellowish-white gelatinous precipitate of $PdCy_2$, readily soluble in KCy and in ammonia. Slightly soluble in HCl. It leaves on ignition spongy metallic palladium. (Characteristic reaction.)

NH_4Cl does not precipitate palladium salts. (Difference from platinum.)

KCl precipitates a brownish-red octahedral double chloride, $2KCl,PdCl_2$, insoluble in absolute alcohol; soluble in water to a dark-red fluid.

NH_4SCN gives no precipitate even after the addition of SO_2. (Distinction from Cu.)

$SnCl_2$ produces a brownish-black precipitate, soluble in HCl to an *intense green solution*.

An iodine solution stains palladium black, but has no effect on platinum.

Palladious salts are reduced to the metallic state by phosphorus, H_2SO_3,KNO_2, formic acid, metallic zinc or iron, alcohol, and other organic compounds.

Palladious chloride, obtained by dissolved PdS in boiling HCl is precipitated by ammonia as flesh-coloured palladammonium chloride, $Pd(NH_3)_2Cl_2$, soluble in ammonia to a colourless fluid from which HCl reprecipitates it as a yellow crystalline chloride, identical in composition.

All palladium compounds are decomposed when ignited.

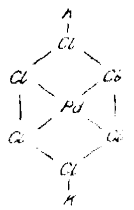
* Palladium shows a very strong tendency to form compounds containing NH_2 (or NH_3) (?). A great number of these are known. It is a point of resemblance to copper and cobalt. Undoubtedly they are amines—that is, derivatives of ammonia in which one or more hydrogen atoms from one or more molecules of NH_3 have been replaced by the metal. Some of the hydrogen atoms in NH_3 seem to be decidedly labile. The solution in ammonia (above) is faintly blue, like copper, but fades rapidly, a pallad ammonium hydrate, $PdN_2H_6(OH)_2$, being formed. This forms a series of salts with acids, as $PdN_2H_6 2HCl = \diagup NH_3HCl$

PALLADIC SALTS.

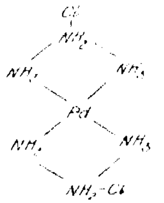
$PdCl_4$ is known only in solution. It is obtained when the metal is dissolved in aqua regia or when the oxide PdO_2 is dissolved in strong HCl. $PdCl_4 2NH_4Cl$ is formed as a bright red almost insoluble crystalline powder when NH_4Cl is added to the $PdCl_4$ solution and boiled, or when a palladious salt, as PdN_2O_6 is boiled with HCl and NH_4Cl added.

KHO added to the $PdCl_4$ solution or the $PdCl_4 2KCl$ solution and boiled gives a black precipitate of PdO_2. In the cold a brown hydrated oxide is formed. This oxide dissolves very slowly in HCl, sometimes giving off free chlorine.

The double chloride above mentioned is probably



and a number of amines are no doubt similarly constituted.



Palladic sulphide also forms double salts with alkaline and other sulphides.

2. **RHODIUM,** Rh″, ^{iv}, and ^{vi}, also a pseudo-triad. Atomic weight, 104·06.—Found in small quantity in platinum ores, and *frequently to a considerable extent in platinum residues, that is the* insoluble portion after treating the platinum mineral with aqua regia.

It is a whitish-grey metal, less ductile than platinum, and scarcely softened, even in the flame of the oxy-hydrogen blowpipe. The specific gravity of unfused rhodium is 10·64, that of the pure metal, after fusion, 12·1. Rhodium is unalterable in the air at ordinary temperatures, but oxidises at a red heat. It also combines with chlorine at a red heat. When pure and in a compact state it resists the action of the strongest acids, even of aqua regia; but when

alloyed with other metals, as with Pb, Bi, Cu, and Pt, it is soluble in aqua regia; when, however, alloyed with Au or Ag it does not dissolve. It is oxidised by fusion with dry potassium hydrate and nitre. Fusion with hydrogen potassium sulphate converts it into soluble potassium rhodic sulphate, $K_6Rh_2(SO_4)_6$. Mixed with sodium chloride and ignited in a current of chlorine, a double chloride of sodium and rhodium, $3NaCl,Rh'''Cl_3 12OH_2$ (?), is formed, which is likewise easily soluble in water, forming a rosy red solution. Hydrogen is absorbed by rhodium powder even to a greater extent than by palladium. This form of the metal also decomposes the vapour of several carbon compounds, as ethylene, acetylene, &c.

Rhodium forms several oxides, chlorides, sulphides, &c., in which the metal exists as a dyad, tetrad (pseudo-triad), or hexad element, thus:

	Oxides.
Rhodious oxide	RhO
Rhodic ,, ...	Rh_2O_3.
,, dioxide	RhO_2.
Rhodic trioxide (anhydride, acting as a weak acid)	RhO_3.
,, tetrahydroxide	$Rh(OH)_4$

	Chlorides.		Sulphides.
Rhodious chloride .	$RhCl_2$	Rhodious sulphide	RhS.
Rhodic chloride .	$RhCl_3$ or Rh_2Cl_6.	Rhodic ,,	Rh_2S_3.

The most important compounds are the Rh_2Cl_6 and Rh_2O_3. Rhodium salts are obtained with difficulty, owing to the insolubility of the metal and its oxide in acids. Their solutions are generally rose-coloured.

REACTIONS IN SOLUTION.

Employ a solution of potassio-rhodic sulphate, or of the double chloride of sodium and rhodium.

Soluble sulphides precipitate from a hot solution brown rhodic sulphide, Rh_2S_3, insoluble in ammonia sulphide, but soluble in boiling nitric acid.

KHO, or NaHO, gives with the chloride a yellowish-brown precipitate of rhodic hydrate, $Rh_2(HO)_6$, soluble in excess; in other rhodic salts this precipitate appears only on boiling.

From a solution of rhodic chloride, KHO, producing at first no precipitate, gives on the addition of alcohol, a brown precipitate of rhodic hydrate.

NH_4OH gives also a yellow flocculent precipitate, only formed, however, after some time, soluble in HCl, forming a rhodamine salt.

KI produces a slight yellow precipitate.

Metallic zinc precipitates black metallic rhodium.

KNO_2 (potassium nitrite) gives with the chloride an orange-yellow precipitate, which is slightly soluble in water, and only very slowly decomposed by strong HCl; characteristic.

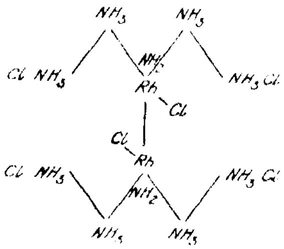
Rhodium is distinguished from the other platinum metals by its insolubility in aqua regia, its solubility in fusing $KHSO_4$, and the behaviour of its chloride with potash and alcohol.

Rhodium exhibits even a greater power than palladium to form amines or rhodium bases. A great number of these have been made, but there is still no certainty as to their constitution. Some are colourless, others rosy-red, and others again of a more or less marked purple colour.

The following are cited as types only of some of these:

Roseo-rhodium chloride =	$Rh_2 10NH_3Cl_6(H_2O)_2$
Luteo ,, ,,	$Rh_2 12NH_3Cl_6$
Purpureo ,, ,,	$Cl_2(Rh_2 10NH_3)Cl_4$

The constitution of this last class may possibly be expressed by:



3. **OSMIUM,** Os'', iv, vi, and viii, also a pseudo-triad. Atomic weight, 198·49.—Found chiefly as a natural alloy of osmium iridium in platinum ores, which remains behind undissolved, when the ores are treated with aqua regia, in the form of white, metallic-looking, hard grains. This alloy is attacked by mixing it with common salt, or potassium chloride, and exposing it in a glass or porcelain tube to a current of moist chlorine gas. Osmic acid is formed, which volatilises, and can be condensed and fixed by passing the fumes into a solution of caustic potash. (Iridium remains behind in the tube as a double chloride, $2KCl,IrCl_4$. This salt is obtained in reddish-black regular octahedra, by recrystallisation from water.) The alkaline solution is evaporated with excess of sal-ammoniac, and leaves on ignition of the dry residue, and extraction with water, metallic osmium, as a black or grey powder, and with metallic lustre. The densest metal has a specific gravity of 21·4. Intense white heat volatilises the metal, but does not melt it. In contact with air, it burns the more readily the finer the metal is divided, and is converted

into *osmic anhydride*, $Os^{viii}O_4$. Red fuming nitric acid, or aqua regia, dissolves osmium likewise, and oxidises it to OsO_4. Very intensely ignited, osmium is rendered insoluble in acids, and has to be fused with nitre, and then distilled with nitric acid, when OsO_4 distils over.

Osmium combines with oxygen, or chlorine, &c., in several proportions, thus:

Osmious oxide .	OsO	Osmious chloride .	$OsCl_2$
Osmic " .	Os_2O_3	——	—
Osmic dioxide .	OsO_2	Osmic tetrachloride	$OsCl_4$
Osmious anhydride	OsO_3	——	—
Osmic anhydride .	OsO_4	——	—

The two highest oxides combine with bases, and form osmites and unstable osmates. OsO_4 is remarkable for its peculiar, exceedingly irritating, and offensive odour, resembling that of Cl and I. It attacks the eyes and the air passages, and is excessively poisonous. It is absorbed by water, and is precipitated from its solutions by all metals, even by mercury and silver, as a black metallic powder. On heating a mixture of finely divided osmium, or of the sulphide, with potassium chloride in a stream of chlorine gas, a double chloride, $Os_2Cl_6,6KCl,3OH_2$, is obtained, which crystallises from water in dark red-brown, regular octahedra. The salt is insoluble in alcohol.

The solution of this double chloride is more stable than that of the osmium chlorides, and may conveniently be employed for studying the reactions.

REACTIONS IN SOLUTION.

SH_2, or sulphides, give a brownish-black sulphide, OsS_4 which only separates when a strong acid is present. The precipitate is *insoluble in ammonium sulphide.*

Alkalies or their carbonates, produce a brownish-red precipitate of hydrated osmic dioxide, $Os(HO)_4$.

On fusing the double chloride with Na_2CO_3, dark grey OsO_2 is obtained.

Heated with tannic acid, or alcohol, with addition of HCl, the double chloride is reduced to the blue osmious chloride, $OsCl_2$

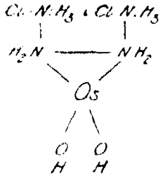
A solution which contains osmic acid (and osmate) is remarkable for its great oxidising power. It decolorises indigo solution, separates iodine from KI, converts alcohol into aldehyde and acetic acid. Sodium sulphite yields a deep violet coloration and dark blue osmious sulphite, $OsSO_3$, gradually separates. Ferrous sulphate produces a black precipitate of OsO_2. Stannous chloride produces a brown precipitate, soluble in HCl to a brown fluid. All compounds of osmium yield the metal when ignited in a current of hydrogen.

This metal also forms amine bases, but not quite so markedly as

is the case with either Pd or Rh. One has been described by Gibbs and Genth as $OsO_2Cl_2N_4H_{12}$. The formula given by Claus is

$$OsCl_2\,4NH_3 + 2H_2O$$

probably



RUTHENIUM, Ru'', ^{iv}, ^{vi}, and ^{viii}, also a pseudo-triad. Atomic weight, 103·5.—Found in small quantity only, in that portion of the platinum ores which remains behind after treating with aqua regia. It is a greyish-white metal, closely resembling iridium, and very difficultly fusible. When heated in the air it becomes covered with bluish-black ruthenic oxide, Ru_2O_3, insoluble in acids. When pure it is insoluble in acids, being scarcely acted upon by aqua regia; fusion with hydrogen potassium sulphate is even without action upon it.

It is attacked either by fusion with caustic potash and nitre, or potassium chlorate, and is converted thereby into potassium ruthenate, K_2RuO_4, a dark green mass, soluble in water to an orange-coloured fluid, which tinges the skin black, from separation of black ruthenic oxide. Acids (HNO_3) throw down the black hydrate.

Or it may be rendered soluble by ignition with potassium chloride in a current of chlorine gas, being thus converted into potassium ruthenic chloride, $2KCl,Ru^{iv}Cl_4$.

Ruthenium forms several oxides, chlorides, &c., thus:

Ruthenious oxide	.	RuO	Ruthenious chloride .	$RuCl_2$
Ruthenic ,,	.	Ru_2O_3	Ruthenic chloride . .	Ru_2Cl_6
Ruthenic dioxide	.	RuO_2	Ruthenic tetrachloride .	$RuCl_4$
Ruthenic trioxide (anhydride)	.	RuO_3	(known only in combination)	
			Ru_2O_5 (also known only in combination)	
Ruthenic tetroxide (perruthenic anhydride)	.	RuO_4		

REACTIONS IN SOLUTION.

A solution of ruthenic chloride, Ru_2Cl_6, prepared by dissolving in HCl the ruthenic hydrate, precipitated by nitric acid from a solution of potassium ruthenate, may be used. It forms an orange-yellow-coloured solution, which on heating is resolved into HCl and Ru_2O_3.

SH_2 produces at first no precipitate, but after some time the fluid acquires an azure-blue tint, and deposits brown ruthenic sulphide, Ru_2S_3. This reaction is very delicate and characteristic.

DRY REACTIONS.

...ic anhydride, when heated on charcoal in the outer flame, ...and is then partly volatilised and forms a yellow crystal ...ate on the charcoal which turns white on cooling; in the ...it is reduced to the metallic state (even without Na_2CO_3); ...*an be obtained as a grey powder on levigating the char-*...

...th borax, all oxides of molybdenum give in the outer flame ...ch is yellow when hot, and colourless on cooling; in the ...e, a dark-brown bead, which is opaque when excess of ...um has been used.

REACTIONS IN SOLUTION.

...y a solution of ammonium molybdate.

...lkaline molybdates are soluble in water. Most others are ...nsoluble.

... or hydrochloric acid precipitates white molybdic acid, H_2MoO_4, from a concentrated solution of a molybdate, ...oluble, however, in a large excess of the acid.

...H_2 gradually precipitates from acidulated solutions brownish-black molybdic trisulphide, MoS_3, soluble in alkaline sulphides or sulpho-salts, which are decomposed again by acids with precipitation of MoS_3, especially on the application of heat. On the addition of a little SH_2 only, the molybdate solution acquires at first a blue tint; added in larger quantities it produces a precipitate, and the supernatant fluid appears green, till on the addition of excess of SH_2 the whole of the metal separates, though slowly, as a trisulphide.

...$H_4)_2S$ gives a similar precipitate, soluble in excess.

...ducing agents, such as $SnCl_2$, $Hg_2(NO_3)_2$, Zn and HCl, &c., produce changes, marked by alterations in colour to lower oxides.

...e principal and most characteristic reaction for molybdic anhydride consists, however, *in precipitating it in a nitric acid* solution, as yellow phospho-molybdate, or arsenio-molybdate, by the addition of a mere trace of soluble phosphate or arsenate.

...TELLURIUM, Te'', ^{iv}, and ^{vi}. Melting point, 452–455° C. ...mic weight, 125.—Occurs in a few places, and in small quantities ... native (graphic and foliated tellurium); more often in combi...on with Au, Ag, Bi, Pb, as a (sulpho) -telluride, analogous to ...hides, &c.; or as tellurous acid, in combination with metallic ...s.

...ellurium exhibits all the physical properties of a metal, and ...nbles antimony in its general appearance. It is a white, brittle ...readily fusible body, which may be sublimed in a glass tube. ...n heated in the air it burns with a greenish-blue flame, emitting

thick white fumes of tellurious anhydride, TeO_2. It is insoluble in HCl, but dissolves readily in HNO_3, forming TeO_2, a white substance which fuses to a yellow fluid, at a gentle heat, and volatilises on stronger ignition in the air. Tellurous anhydride scarcely dissolves in water, and the solution does not redden litmus; readily in HCl, less so in HNO_3. It also dissolves freely in potash or soda, slowly in ammonia, forming alkaline tellurites. On dilution with water, white tellurous acid, H_2TeO_3, is precipitated from an acid solution. A nitric acid solution slowly deposits crystalline tellurous anhydride, even without the addition of water.

Tellurium forms several oxides, chlorides, sulphides, &c., in which the metal is a dyad, tetrad, or hexad; thus:

	Oxides.
Tellurous oxide (anhydride)	TeO_2
,, acid	H_2TeO_3
Telluric oxide (anhydride)	TeO_3
,, acid	H_2TeO_4

	Chlorides.	Sulphides.
Tellurous, or dichloride . . .	$TeCl_2$	—
Telluric, or tetrachloride . .	$TeCl_4$	TeS_2
	—	TeS_3

It also forms with hydrogen a gaseous compound (telluretted hydrogen or hydrotelluric acid), TeH_2 (analogous with SH_2, and SeH_2).

Both the di- and tri-oxides are capable of forming with metallic substances basic salts called tellurites and tellurates. The alkaline and alkaline earthy tellurites—formed by fusing tellurous acid with the carbonates of these metals—are all more or less soluble in water; all others obtained by double decomposition are insoluble. The tellurates of the alkali metals, prepared in like manner, are also soluble in water; the others are insoluble. They can be prepared by double decomposition.

The sulphides of this element act as sulpho-acids, forming, with the alkaline sulphides, sulpho-tellurites and tellurates.

DRY REACTIONS.

When tellurites or tellurates are heated with charcoal and K_2CO_3, they are reduced to potassium telluride, TeK_2, which produces a black stain on a moist silver plate, and is soluble in water, forming a dark-red solution. When HCl is added to this solution, hydrotelluric acid gas, TeH_2, is evolved, resembling SH_2 in smell and soluble in water, to a pale-red solution, which is decomposed in contact with air, with deposition of tellurium.

All compounds of tellurium are readily reduced on charcoal in the inner flame. The reduced element is volatilised and forms a white scarcely visible deposit of tellurous anhydride on the char-

coal. Stannous chloride colours it black, owing to the separation of tellurium.

With borax or microcosmic salt a clear colourless bead is obtained, which, when heated on charcoal, is rendered grey and opaque, owing to reduced element.

REACTIONS IN SOLUTION.

A. **TELLURIC COMPOUNDS.**—Use a solution of potassium tellurate, K_2TeO_4 (obtained by fusing potassium tellurite with nitre).

HCl does not decompose tellurates in the cold, but on boiling the solution, chlorine is evolved, and on dilution with water tellurous acid, H_2TeO_3, is precipitated, soluble only in a considerable excess of HCl. (Distinction of TeO_3 from TeO_2.)

B. **TELLUROUS COMPOUNDS.**—Use a solution of potassium tellurite, K_2TeO_3.

HCl decomposes this solution and precipitates white tellurous acid. Tellurium resembles in this respect Sb and Bi compounds.

SH_2 precipitates from acid solutions brown tellurous sulphides, TeS_2, resembling in colour SnS, and very freely soluble in ammonic sulphide.

Reducing agents, *e.g.*, Na_2SO_3, $SnCl_2$, metallic zinc and HCl, a solution of sulphurous acid, &c., reduce tellurium compounds and precipitate black tellurium, which is insoluble in an aqueous solution of potassium cyanide.

4. **SELENIUM,** Se'', ^{iv}, and ^{vi}. Varieties α and β. Atomic weight, 78·8. Specific gravity, $\alpha = 4·8$; $\beta = 4·2$. Melting point $\alpha = 217°$ C.; $\beta = 125–130°$ C. Boiling point, α-Se = 67·6–68·3° C. $\beta = 66·4–66·6°$ C.—Occurs in the free state at Culebras, Mexico, in crystals sometimes called riolite from Del Rio, who discovered it. It is also found in certain iron and copper pyrites, and where these are used for the manufacture of sulphuric acid, a red deposit of selenium is found in the chambers. It is found also as selenides of Pb, Cu, Hg, Ag, Fe, &c. Selenium, like sulphur, occurs in different allotropic states, amorphous and crystalline. The crystalline or α-selenium is insoluble in CS_2; β or amorphous selenium is soluble in CS_2.

Reactions.—Heated in air it burns with a bluish flame and forms selenious anhydride, SeO_2, whilst at the same time a disagreeable odour like decaying horse-radish is given off. The same oxide is formed when selenium is dissolved in nitric acid or aqua regia.

It combines directly with bromine and chlorine, and also when heated with iodine, sulphur, phosphorus, and metals.

Selenium conducts electricity slightly; exposure to light increases

its conducting power; when heated its conducting power decreases.

This remarkable property of selenium may probably be made use of for photometrical purposes.

It dissolves in strong sulphuric acid, forming a green solution, from which water precipitates the element as a red powder.

Selenites containing selenic anhydride, SeO_3, are formed by heating selenium or its compounds with carbonates and nitrates of the alkalies. These oxides form two series of salts, viz., selenites and selenates. The selenites are the more stable of the two.

DRY REACTIONS.

Selenium compounds are reduced, when heated with Na_2CO_3 on charcoal, in the inner blowpipe flame, and may be readily recognised by the characteristic smell of horse-radish which they give off. If the saline residue, which contains sodium selenide, $SeNa_2$, be placed on a bright silver coin and moistened with a drop of water, a black stain is produced on the silver. Treated with dilute HCl, it evolves gaseous hydroselenic acid (selenietted hydrogen) SeH_2, analogous in composition and properties to sulphuretted hydrogen. It is an inflammable, fœtid, poisonous gas, very soluble in water. The aqueous solution of SeH_2 gradually deposits selenium on exposure to air; it precipitates selenides from solutions of many metallic salts.

REACTIONS IN SOLUTION.

A. **SELENIC COMPOUNDS.**—Use a solution of potassium selenate, K_2SeO_4.

Selenates are stable salts, closely resembling the sulphates. They are soluble in water with the exception of the barium; strontium, calcium, and lead salts, which are insoluble in water and in dilute acids.

HCl decomposes selenates, on boiling; chlorine is evolved, and the salt is reduced to a selenite. (Distinction from SeO_2.)

SH_2 does not produce a precipitate, till the selenate has been reduced to selenite, by boiling with HCl.

$BaCl_2$ produces a white precipitate of barium selenate, $BaSeO_4$, insoluble in water and in dilute acids; decomposed by boiling HCl.

B. **SELENIOUS COMPOUNDS.**—Use a solution of an alkaline selenite.

The *normal alkaline selenites are soluble in water, most others* are insoluble; nearly all acid selenites are soluble. HCl dissolves but does not decompose selenites.

SH_2 produces from an acid solution of a selenite, a lemon-yellow precipitate of selenious sulphide, SeS_2 (?), which almost immediately breaks up into its component elements $Se + S_2$, but is readily soluble in ammonium sulphide.

$BaCl_2$ gives a white precipitate of barium selenite, $BaSeO_3$, soluble in dilute HCl or HNO_3.

Reducing agents, such as SO_2, alkaline sulphites, $SnCl_2$, metallic Zn, and Fe, precipitate selenium from acidulated (HCl) solutions, as a red powder, which turns grey at high temperatures, and is soluble in KCy solution. ($FeSO_4$ is without action.) Metallic copper is immediately coated black when placed in a warm solution containing hydrochloric acid, and on standing the solution turns light red, from separation of amorphous selenium.

5. **GERMANIUM**, Ge″ and ^{iv}.—This metal was discovered by C. Winckler in *argyrodite*, which is a sulphogermaniate of silver.

The metal is silvery-white and brittle, it melts at about 900° C., and volatilises at a little higher temperature. Its specific gravity is 5·47 and its specific heat 5·4. Dry chlorine combines with the metal and forms $GeCl_4$, a colourless liquid that boils at 86° C., fumes in the air, and is decomposed by water. HNO_3 acts on the metal and gives a white oxide; H_2SO_4 dissolves it, and by evaporation of the solution and ignition of the residue GeO_2 is obtained; HCl is without action upon it.

GeO is a greyish-black powder soluble in HCl. This solution of germanous chloride gives a yellow precipitate with alkalies, a white precipitate with K_4FeCy_6, and a reddish brown precipitate with H_2S. It reduces permanganates and gold and mercury salts.

Acid solutions of GeO_2 give a white precipitate of GeS_2 by the action of SH_2. The precipitate is soluble in ammonium sulphide.

Group I. comprises the rare metals precipitable by HCl, viz., the metal tungsten, or wolfram, which is precipitated as tungstic acid, H_2WO_4, and thallium precipitated as thallous chloride, TlCl. Several other metals already treated of in Group III. besides thallium, viz., niobium, tantalum, molybdenum, are likewise precipitated, but the precipitated acids ($HNbO_3$, $HTaO_3$, and H_2MoO_4) dissolve again in an excess of hydrochloric acid.

TUNGSTEN, or **WOLFRAM**, W^{iv} and ^{vi}. Atomic weight, 183·6.—This metal occurs in nature as trioxide in the form of tungstates, in combination with the bases CaO, FeO, MnO, in the minerals wolfram, Fe″(Ca)WO_4, and $CaWO_4$, scheelite, &c.

The metal can be obtained by intensely heating the oxide in a current of hydrogen, or combined with some carbon by fusion in the electric furnace. It forms an iron-grey powder, of specific gravity 19·12, very difficultly fusible, and becomes again oxidised to tungstic anhydride, WO_3, when heated in air. Dry chlorine gas converts it into dark violet, WCl_6, which sublimes, and a more volatile red compound, WCl_4. Both chlorides are decomposed by water into the corresponding hydrates, with formation of HCl. The metal is insoluble, or scarcely soluble, in acids, even in aqua regia.

The following are some of the more important compounds which tungsten forms with oxygen, chlorine, and sulphur:

	Oxides.	Chlorides.	Sulphides.
Tungstic anhydride (lemon-yellow) .	WO_3	WCl_6	WS_3
Tungstic dioxide (brownish-black) .	WO_2	WCl_4	
Intermediate (blue-coloured) oxide .	W_2O_5 $= WO_2,WO_3$	WCl_5 WCl_4,WCl_6	

Tungstic anhydride can be prepared from wolfram or tungsten, by digesting the finely divided mineral in aqua regia, till it is completely decomposed, and evaporating to dryness on a water bath. The metallic chlorides are dissolved out with acidulated water, and the residue, which contains a little silica and sometimes niobic acid, washed with alcohol and treated with ammonia. Tungstic acid is dissolved, and silicic and niobic acids are left behind. From the ammonia salt, pure anhydride is obtained by the evaporation of the filtrate and ignition.

DRY REACTIONS.

When heated on charcoal in the reducing flame, together with Na_2CO_3 and KCy, tungstic anhydride is reduced to a black powder, *containing metallic tungsten. Heated with microcosmic salt* tungsten compounds give a colourless bead in the outer flame; in the inner flame a blue bead, which, on the addition of a little $FeSO_4$, changes to blood-red. The addition of tin changes the red bead to blue or green.

REACTIONS IN SOLUTION.

A solution of sodium tungstate, Na_2WO_4, may be used.

The alkaline tungstates are soluble in water, all others are insoluble, and can be obtained by double decomposition.

Mineral acids (HCl, HNO_3, H_2SO_4) precipitate white tungstic acid, H_2WO_4. It turns yellow on boiling, and is quite insoluble in excess of the acids. (Distinction from MoO_3.) Non-volatile acids (*e.g.*, phosphoric, tartaric) precipitate it likewise, but the precipitate is soluble in excess. It is also readily soluble in ammonia.

SH_2 produces no precipitate from an acid solution, but reduces the tungstic acid to the blue oxide, W_2O_5.

$(NH_4)_2S$ produces no precipitate from alkaline tungstates, but on acidulating with HCl, light brown tungstic trisulphide, WS_3, is precipitated, slightly soluble in pure water, but insoluble in the presence of salts. The solution is coloured blue. The precipitated sulphide dissolves readily in ammonium sulphide.

$SnCl_2$ gives at first a yellow precipitate; on acidulating with HCl and applying heat, the precipitate acquires a beautiful blue colour. This reaction is very delicate and highly characteristic.

Zinc sub-sulphite, obtained by treating a sulphite with zinc, reduces tungsten compounds to a deep brown tungstous oxide of unknown composition; in small quantities a deep blue colour only may be produced.

Sodium tungstate is used commercially for rendering fabrics difficultly combustible so that they will not burn with flame.

GALLIUM, Ga''' Atomic weight, 69·9. Specific gravity in the solid state 5·956 at 24·5 C., that of the liquid at the same temperature is 6·069°. Melting point 30·1°.

This metal was discovered in the zinc blende of Pierrefitte in the valley of Argeles, Hautes Pyrenees, but is contained in greater abundance in that from Asturia, and still more so in the black blende of Bensberg (Rhine); it has also been found in exceedingly minute quantities in blende from other localities.

Gallium is a hard metal of a greyish-white colour, which tarnishes slightly in moist air. When melted it adheres to glass, forming a whiter mirror than that produced by mercury. It remains in a state of superfusion with great facility, a globule of it may remain liquid for an indefinite period; it possesses some malleability, and may be cut with a knife. Metallic gallium is obtained by subjecting the pure oxide or basic sulphate dissolved in a solution of potassium hydrate to electrolysis, when it is deposited in the liquid state on the negative platinum electrode, which should be very much smaller than the positive electrode.

Heated to redness the metal does not volatilise appreciably, but becomes coated with a film of oxide. It is scarcely attacked by nitric acid in the cold, but dissolves readily when heated with hydrochloric acid; a solution of potassium hydrate dissolves it with evolution of hydrogen.

Extraction of Gallium from its Ores.—The blende is digested in aqua regia, 5 parts hydrochloric, 1 part nitric, the solution is then boiled to expel the greater part of the nitric acid, and slips of pure zinc are immersed in the solution, and withdrawn when the evolution of hydrogen has almost, but not entirely, ceased; by this means the Cu, Pb, Cd, Ir, Tl, Ag, Hg, Se, As, &c., are for the most part removed. A large excess of zinc is added to the clear fluid, which is then boiled for some hours; a bulky gelatinous precipitate then comes down, consisting of alumina, basic salts of zinc, and gallium. This precipitate is redissolved in hydrochloric acid, ammonium acetate is added, and the metals precipitated with sulphuretted hydrogen. The solution in hydrochloric acid of the white sulphides is fractionally precipitated with sodium carbonate; the gallium is found in the first portions; the point where the precipitation may be stopped is easily recognised by spectroscopic examination. The gallium is separated from the zinc by solution in sulphuric acid and addition of excess of ammonia. Much of the gallium remains dissolved in the ammonia, which is recovered by boiling till excess of ammonia is expelled; the excess of ammonia salts is then decom-

solution. If this solution is allowed to stand for twelve hours, and then heated to 150° for a short time, and after cooling a drop of HNO_3 of density 1·2 is added on a porcelain plate, a coloration is observed, which is sometimes violet at first changing to blood-red, and then yellow.

A solution of molybdic acid, Frohde's reagent,* or a molybdate of an alkali in strong H_2SO_4, added to morphine or a dry salt of morphine on a porcelain plate, gives a deep violet colour at once; this colour gradually changes to olive-green, and then to a deep blue on stirring. If a small quantity of morphine be dissolved in about 1 cc. of concentrated HCl, a drop of strong H_2SO_4 added, and the mixture heated on the water-bath until the HCl is driven off, a purplish residue is obtained. This residue is treated with a little HCl, and neutralised with a cold saturated solution of $HNaCO_3$, and then one drop of an alcoholic solution of iodine added—the liquid becomes emerald-green. On shaking with ether the substance (apomorphine) is dissolved to a violet-red solution. Fe_2Cl_6 gives, with strong solutions of morphine salts, a dark-blue coloration which is destroyed by the addition of acids; excess of ferric chloride should be avoided.

II. NON-VOLATILE ALKALOIDS, PRECIPITATED BY KHO OR NaHO, INSOLUBLE IN EXCESS, ALSO PRECIPITATED BY $HNaCO_3$, EVEN FROM ACID SOLUTIONS.

NARCOTINE, $C_{22}H_{23}NO_7$.

Narcotine is found together with morphine in opium. It is insoluble in water, and only sparingly soluble in alcohol, ether, and light petroleum. It is easily soluble in benzene, but its best solvent is chloroform. Narcotine melts at 176°. All narcotine salts possess an acid reaction.

Any salt of narcotine may be employed for the reactions.

All alkalies, their carbonates and bicarbonates, precipitate narcotine immediately in the form of a white powder, crystalline under the microscope.

Concentrated HNO_3 dissolves narcotine on warming with evolution of nitrous fumes, and forms a reddish-yellow solution; on heating more strongly more fumes are given off, and the solution becomes yellow.

Concentrated H_2SO_4 dissolves narcotine with a pale greenish-yellow colour changing to pure yellow. On heating in a porcelain dish, the solution becomes orange-red and violet-blue at the edge, and when the sulphuric acid begins to evaporate, it assumes a dirty reddish-violet colour.

If a small quantity of narcotine be dissolved in Erdmann's reagent,† a brownish colour is first formed, becoming red.

Frohde's reagent * dissolves narcotine, forming a green solution.

* 0·005 grm. of sodium molybdate dissolved in 1 cc. of concentrated H_2SO_4.

† 6 drops of HNO_3, density 1·25, mixed with 100 cc. of water, and 10 drops of this solution are added to 20 grms. of pure concentrated H_2SO_4.

If the solution, however, contains double the amount of sodium molybdate, the green colour changes to a magnificent cherry-red.

Chlorine water gives a yellow colour, changed by NH_4OH to a yellowish-red.

If a solution of narcotine in strong H_2SO_4 is heated until the red coloration appears, and then Fe_2Cl_6 added, the portions of the liquid in contact with the ferric chloride become red with brilliant violet edges, and after 10 or 15 minutes a cherry-red coloration is produced.

If narcotine or one of its salts be dissolved in dilute H_2SO_4 and MnO_2 added, and the mixture boiled, the alkaloid is oxidised into opianic acid, cotarnine, and CO_2. On filtering and adding NH_4OH, no precipitate is produced.

QUININE, $C_{20}H_{24}N_2O_2$.

Quinine occurs in cinchona barks together with cinchonine and several other bases. It may be obtained crystallised either anhydrous or with three molecules of water of crystallisation. In the hydrated state, it effloresces on exposure to the air. Quinine is sparingly soluble in cold, but more readily soluble in hot water, but still more so in alcohol, ether, chloroform, and carbon disulphide. Crystallised quinine melts at 57° in its water of crystallisation, which it loses at 100°; when anhydrous it melts at 177°.

The neutral salts of quinine are sparingly soluble in water; the acid salts, however, are readily soluble, and solutions of many of them, especially the sulphate, exhibit a bluish fluorescence. A solution of quinine sulphate acidulated with dilute H_2SO_4 turns *the polarised ray strongly to the left. (Distinction from cinchonine.)*

The alkalies and their normal carbonates precipitate quinine from not too dilute solutions in the form of an amorphous powder which soon becomes crystalline, as seen, under the microscope. If a salt of quinine be precipitated by means of ammonia, ether (containing 2 per cent. of alcohol) added, and the mixture shaken, the precipitated quinine redissolves in the ether, and the clear liquid forms two layers. Quinine may be separated from cinchonine by this process.

$HNaCO_3$ forms a precipitate only from moderately strong solutions; the precipitate is somewhat soluble in excess, and contains carbonic acid.

Strong HNO_3 dissolves quinine to a colourless solution, becoming yellowish on heating. A nitro-derivative is formed.

Chlorine water (about one-fifth its volume) added to a solution of a quinine salt does not colour the solution, but on the addition of NH_4OH in excess, an intense emerald-green colour is produced. If after the addition of chlorine water some solution of K_4FeCy_6 is added, and then a few drops of ammonia, the solution acquires a deep red tint, speedily changing to a dirty brown. The red colour is destroyed by an acid, but may be reproduced by the cautious

addition of NH_4OH. This reaction is most characteristic, but is interfered with by the presence of morphine.

If quinine sulphate is dissolved in a little acetic acid, alcohol added, and then sufficient alcoholic solution of iodine to colour the liquid brownish, the sulphate of iodoquinine (herapathite) separates out after a short time as a black crystalline powder, or in the form of plates, which are beautifully dichroic, and polarise light strongly. This reaction is very characteristic, and by the employment of the microscope very delicate.

Concentrated H_2SO_4 dissolves quinine and its salts, forming a colourless or faintly yellow solution; on heating the colour changes to yellow and afterwards to brown. Erdmann's reagent only gives a faint yellow colour.

CINCHONINE, $C_{19}H_{22}N_2O$.

Cinchonine occurs *in cinchona bark, together with quinine and* other alkaloids. It forms either transparent, brilliant rhombic prisms or fine white needles, or, if precipitated from concentrated solutions, a loose white powder.

Cinchonine is almost insoluble in both hot and cold water. It is but sparingly soluble in cold alcohol, but somewhat soluble on boiling, from which solution most of the *cinchonine crystallises on cooling*. It is almost insoluble in ether, chloroform, and light petroleum, but dissolves readily in chloroform mixed with one-fourth or one-third of its bulk of alcohol.

When cinchonine is cautiously heated it melts, and gives off white fumes, which condense upon cold surfaces in the form of small brilliant needles, or as a loose sublimate, a peculiar aromatic odour being exhaled at the same time.

Cinchonine salts are in general more soluble than the corresponding quinine compounds. The solutions are not fluorescent, and turn the flame of the polarised ray to the right.

Alkalies and their normal carbonates immediately precipitate amorphous cinchonine, insoluble in excess.

$HKCO_3$ and $HNaCO_3$ give the same precipitate.

Concentrated H_2SO_4 dissolves cinchonine, forming a colourless liquid, which on warming becomes first brown, and finally black; the same change of colour is noticed on the addition of HNO_3.

Chlorine water causes no changes of colour, but on adding NH_4OH a yellowish-white precipitate is produced.

If K_4FeCy_6 is added to a neutral solution of a cinchonine salt, a yellowish flocculent precipitate of cinchonine ferrocyanide is formed. On the addition of excess of the precipitant, and on gently and slowly heating, the precipitate dissolves, but separates on cooling in brilliant gold-yellow scales, or in long needles, often aggregated in the shape of a fan. With the aid of a microscope this reaction is most delicate and characteristic.

Quinine and cinchonine may be separated from narcotine by repeatedly shaking up the acidified solution with chloroform; the

chloroform is then separated, and ammonia and ether containing 2 per cent. of alcohol added to the aqueous solution, when the cinchonine separates out, and the quinine dissolves in the ether. The alkaloids may then be readily tested by the reactions given above.

III. Non-Volatile Alkaloids, Precipitated by KHO or NaHO, Insoluble in Excess; not Precipitated by $HNaCO_3$.

STRYCHNINE, $C_{21}N_{22}N_2O_2$.

Strychnine is found, together with brucine, in the fruit of the *Strychnos nux-vomica* and *Strychnos ignatii.* It occurs either in white, brilliant, rhombic prisms, or as a white powder. It possesses an alkaline reaction, and is intensely bitter. Strychnine is almost insoluble in water, absolute alcohol, ether, and light petroleum. It is slightly soluble in ether containing water and alcohol, amyl alcohol and benzene, but very readily soluble in chloroform.

Strychnine does not melt without decomposition, but by careful heating small quantities may be sublimed unchanged.

Most salts of strychnine are soluble in water and alcohol, insoluble in ether, chloroform, amyl alcohol and benzene. All the salts taste intensely bitter, and are very poisonous.

KHO, NaHO, and Na_2CO_3 precipitate strychnine as a white crystalline powder, insoluble in excess.

NH_4OH gives the same precipitate soluble in excess; after a short time, however, the strychnine crystallises from its solution in ammonia in the form of needles. $HNaCO_3$ added to a neutral solution of a strychnine salt precipitates the alkaloid in the form of fine needles, insoluble in excess. If, however, a drop of acid be added, so as to form free carbonic acid, the precipitate is redissolved, although the solution may still be alkaline. As the free carbonic acid escapes on exposure to the air, the strychnine is gradually reprecipitated.

KSCN gives immediately from strong solutions, but only after some time from dilute solutions, a white crystalline precipitate, insoluble in excess.

$HgCl_2$ forms a white precipitate consisting of clusters of needles; it is soluble on boiling, but recrystallises on cooling.

If strychnine is dissolved in concentrated H_2SO_4, and then brought into contact with any oxidising agent (such as K_2CrO_4, $K_2Mn_2O_8$, $K_6Fe_2Cy_{12}$, PbO_2, or MnO_2), best in the solid condition, the liquid assumes a magnificent blue-violet colour, which changes to red and then to reddish-yellow. The reaction may be performed by precipitating the strychnine as a chromate by means of K_2CrO_4, freeing the precipitate from moisture as far as possible, and treating it on a watch-glass with strong H_2SO_4, when the blue-violet or blue colour is observed.

The most delicate reagent for strychnine is the green liquid obtained by dissolving 1 part of $K_2Mn_2O_8$ in 2000 parts of strong

H_2SO_4, but under these conditions other organic substances may cause a similar colour to be generated.

This reaction is impaired by the presence of chlorides, nitrates, and large quantities of organic matter, so that the strychnine should be obtained as free as possible from impurities before employing the above test. It should be mentioned that curarine gives the same reaction as strychnine with H_2SO_4 and K_2CrO_4, but a distinction is that the curarine is coloured red by H_2SO_4 alone, and that its coloration with K_2CrO_4 is more permanent than in the case of strychnine.

If a few drops of a solution of ammonium vanadate in 100 to 200 parts of strong H_2SO_4 be added to a little strychnine on a watch-glass and allowed to remain a few moments until the mixture becomes darker in colour, and the watch-glass then slightly inclined, a magnificent blue colour will be seen at the moment the vanadium sulphate solution runs off the residue; this colour soon turns to violet, and then to vermilion or reddish-yellow. If KHO or NaHO be added as soon as the red colour appears permanent a rose or purplish-red colour is produced which becomes more brilliant on dilution. This reaction is not so delicate as the previous one, but has the advantage of scarcely being affected by other organic matter.

Chlorine-water gives a white precipitate, soluble in ammonia, to a colourless liquid. Strong HNO_3 dissolves strychnine and its salts to a colourless solution, becoming yellow when heated.

BRUCINE, $C_{23}H_{26}N_2O_4$.

Brucine occurs together with strychnine in different kinds of strychnos.

It crystallises with four molecules of water in the form either of right rhombic prisms, clusters of needles, or a white crystalline powder.

Brucine is sparingly soluble in cold, but rather more so in hot water. It is readily soluble in alcohol, amyl alcohol, and chloroform, but less so in benzene, and almost insoluble in absolute ether. It possesses an intensely bitter taste.

When heated, brucine fuses with loss of its water of crystallisation, but on careful heating it may be sublimed unchanged. Its solution in alcohol rotates the polarised ray to the right.

KHO, NaHO and Na_2CO_3 precipitate brucine, insoluble in excess. The precipitate when first formed is granular, but may be seen under the microscope to change suddenly into needles with the absorption of water,

NH_4OH produces a whitish precipitate with brucine salts; this precipitate appears to consist of minute oily drops which gradually change with the absorption of water to small needles. The fresh precipitate, before absorption of water, is readily soluble in excess, but brucine soon crystallises from the solution in small groups of needles.

$HNaCO_3$ precipitates, as in the case of strychnine, brucine from neutral solutions of its salts, soluble in free carbonic acid; from acid solutions no precipitate is produced.

Strong HNO_3 dissolves brucine and its salts to an intensely red solution, which afterwards becomes a yellowish red, and yellow on warming. On the addition of $SnCl_2$, or colourless NH_4HS, to the solution, and then heated, an intense violet colour is formed, from concentrated solutions a violet precipitate. With NaHS instead of the above reducing agents the violet colour afterwards changes to green.

Strong H_2SO_4 gives with brucine or one of its salts a pale rose colour which afterwards becomes yellow. Erdmann's reagent gives the same colours.

$Hg_2(NO_3)_2$, as free as possible from acid, gives a colourless solution which on heating on a water-bath gradually assumes a fine carmine colour. (Distinction from strychnine, which gives no colour with $Hg_2(NO_3)_2$.)

Frohde's reagent gives a red, changing to reddish-orange, fading rapidly.

K_2CrO_4 gives a yellowish-red crystalline precipitate after some time.

Chlorine-water added to a brucine salt gives a bright red colour, changed by ammonia to a yellowish-brown.

KSCN gives a granular precipitate from strong solutions at once, from dilute solutions only after some time.

$HgCl_2$ gives a white granular precipitate.

SEPARATION OF STRYCHNINE, BRUCINE, VERATRINE, AND ATROPINE.

Strychnine is separated from the other members of this group by cold absolute alcohol, in which it is insoluble, all the others being readily soluble. The alcoholic solution of brucine, veratrine, and atropine must be diluted with water and shaken up with light petroleum, which dissolves the brucine and veratrine, the atropine remaining in the aqueous solution. If this aqueous solution be shaken up with ether, the atropine is partially dissolved, but leaving the veratrine in solution. This separation of brucine and atropine is not altogether satisfactory, and for confirmation the respective colour tests should be resorted to. Other methods of separation will also be suggested after the foregoing reactions for alkaloids have been gone through, but in no case should the separation by means of different solvents be regarded as conclusive, unless these observations are confirmed by the most characteristic tests for the substances suspected.

It may be here incidentally remarked, that, if the alkaloids to be tested are mixed with various foreign organic matters, they must first be separated by means of precipitation by various general reagents. The reagents which either precipitate all the alkaloids

or most of them are (I) $PtCl_4$; (II) a solution of iodine in KI; (III) potassio-mercuric iodide; (IV) potassio-cadmium iodide; (V) potassio-bismuthous iodide; (VI) phosphomolybdic acid; (VII) phosphoantimonic acid; (VIII) phosphotungstic acid; and (IX) picric acid.

By means of these reagents the alkaloids are precipitated in various states, and suitable methods must then be used to separate the alkaloids from the compounds formed, which will readily be suggested from the reactions of the various precipitants of the above reagents.

Both platinic and auric chlorides unite with alkaloids, or rather with their hydrochlorides, forming double salts, very similar to the manner in which ammonium chloride and chlorides of bases of the aniline type, as $C_6H_5NH_2HCl$, unite with these chlorides.

Most of these combinations can be decomposed by SH_2.

Picric acid combinations are, generally, easily decomposed by ammonia.

APPENDIX IV.

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS.

I. Names of Salts.	II. *Soluble in Water.*	III. Insoluble in water, soluble in, or decomposed by, Acids.	IV. Insoluble in Water and Acids.
Carbonates	Alkaline carbonates, and acid carbonates of Ba, Sr, Ca, Mg, Fe″, Mn, and Pb.	All other carbonates are decomposed by dilute acids, with evolution of CO_2. Spathose iron ore and dolomite are decomposed slowly.	None.
Sulphates	Most sulphates, with the exception of those mentioned in Columns III. and IV. (Ag_2SO_4 is difficultly soluble.)	A few basic sulphates, such as of Hg″, 'Hg'$_2$, Fe^{vi}, Bi‴, Sn″.	The sulphates of Ba, Pb, Sr, Ca, and the red chromic sulphate.
Sulphites	Alkaline sulphites, and the acid sulphites of the alkaline earthy metals.	All other sulphites are decomposed by acids (CO_2 and H_3BO_3 excepted), with evolution of SO_2.	None.
Hyposulphites . .	Most hyposulphites are soluble in water (BaS_2O_3, $Ag_2S_2O_3$, and PbS_2O_3 are but little soluble).	All other hyposulphites are decomposed by acids, with evolution of SO_2 and separation of sulphur.	None.
Sulphides	Alkaline and alkaline earthy sulphides. (CaS and MgS are only sparingly soluble.)	All other sulphides are decomposed by HCl, with evolution of SH_2, or by HNO_3, or aqua regia, with separation of sulphur.	None.
Nitrates	All nitrates, with the exception of a few basic nitrates (Bi, Hg).	A few basic nitrates, which are readily soluble in dilute HNO_3.	None

TABLE SHOWING THE SOLUBILITY OF SALTS IN WATER AND ACIDS—*continued.*

I. Names of Salts.	II. Soluble in Water.	III. Insoluble in Water, soluble in, or decomposed by, Acids.	IV. Insoluble in Water and Acids.
Nitrites	All nitrites. ($AgNO_2$ is somewhat difficultly soluble.)	—	—
Chlorides	Most chlorides, with the exception of those mentioned in Column IV.	[A few oxychlorides].	The chlorides of Ag, Hg_2, [Pb], (Cu_2Cl_2), Au'Cl, Pt''Cl_2. (Comp. reactions of Pt.)
Chlorates	All chlorates.	—	None.
Hypochlorites . . .	All hypochlorites.	—	—
Bromites	Most bromides, with the exception of those mentioned in Column IV.	—	bromides of Ag, Hg_2, [illegible] (less soluble in water than $PbCl_2$), and of 'Cu'$_2$ (soluble in HCl).
Iodides	Most iodides, with the exception of those mentioned in Column IV.	PbI_2, HgI_2 (decomposed into HgI_2 and Hg); Cu_2I_2 decomposed by HNO_3 with evolution of I.	The iodides of Ag, ['Hg'$_2$, Pb, Hg'', and 'Cu'$_2$] (and PtI_2 nearly and PdI_2).
Iodates	The alkaline iodates only dissolve readily in water.	Barium, lead, silver, and other iodates dissolve more or less readily in acids (HNO_3).	None.

Fluorides	The alkaline fluorides and a few others, especially AgF, HgF_2.	The fluorides of the alkaline earthy metals, of lead, and a few other metals.	Fluor spar, decomposed by concentrated H_2SO_4 only.
Phosphates (ortho-) . .	The alkaline phosphates only.	All other phosphates are soluble in acids.	None.
Pyrophosphates . .	Alkaline pyrophosphates.	All others.	None.
Metaphosphates . .	The alkaline and a few metallic metaphosphates.	Most others.	—
Silicates	Potassium and sodium silicates are mostly soluble.	Others are decomposed by acids with separation of $Si(HO)_4$. All silicates are decomposed by HF.	Many natural silicates. (Comp. silicates.)
Borates	The alkaline borates. All others are difficultly soluble in water, but none are absolutely insoluble.	All borates dissolve in acids.	—
Cyanides . . .	The cyanides of the alkali and alkaline earthy metals, as well as $HgCy_2$.	Most other (single) insoluble cyanides *are readily decomposed* by acids.	AgCy is insoluble *in* dilute HNO_3, but is decomposed by aqua regia or hot H_2SO_4.
Ferrocyanides . . .	The alkaline ferrocyanides are readily soluble in water. The others are mostly difficultly soluble or insoluble.	Most others are insoluble in dilute HCl.	The ferricyanides insoluble in acids are decomposed by boiling with aqua regia. Both ferro- and ferri-cyanides are decomposed by boiling with KHO.
Cobalticyanides . .	Cobalticyanides of K, Na, Ba, Sr, Ca, and Mg are soluble; also the salts of Fe^{iv} Hg, and Pb	Most others are insoluble in acids (HCl).	Some (Cu and Ag) are insoluble in acids, but are decomposed by KHO or strong H_2SO_4.

APPENDIX V.

UNFORTUNATELY from time to time several methods of writing the formulæ of chemical substances have been proposed and partly adopted, consequently there are several modes in use, empirical, structural or constitutional, and graphic. All these are useful under certain circumstances. Structural formulæ are almost a necessity when dealing with so-called organic compounds. And, further, it is quite correct to use them always with organic compounds, as in most cases they represent at least one way in which the organic compound can be built up or synthesised. With minerals this is seldom the case; we know little of the "structure" of minerals excepting by analogy. It is, however, desirable that we should, wherever possible, express in a formula the constitution of the compound, for that will, or should, exhibit how and in what manner it will react with another substance.

The formulæ used in this book are, as far as minerals are concerned, empirical, showing only the number of atoms of any particular element united together, and generally the *least possible* number.

By the adoption of a somewhat arbitrary arrangement most of these empirical formulæ may be converted into a "structural" one, in which one idea, at any rate, of the constitution of the substance may be exhibited and the same number of atoms indicated as taking a part by the purely empirical formulæ still retained. Again, from these "structural" formulæ graphic may be formed, by arranging the atoms in space with regard to each other, so that, as far as we at present know, the element in a compound, with the greatest "fixing" or combining power for other elements taking its power in this respect for hydrogen as unity, is considered as the dominating element; and its affinities must be first satisfied before those of other elements come into play.

This may be a correct assumption or only partially so.

The ordinary formula for sulphuric acid is H_2SO_4. It is alone used in this book for simplicity. The action of peroxide of hydrogen on SO_2 shows that it may be considered as $SO_2(OH)_2$. When SO_3 comes in contact with water, H_2O, a direct union, as far as we can see, takes place, and hence the constitution would be H_2OSO_3, unless an internal change takes place. The action of a metal, in presence of water, on sulphuric acid is to expel two hydrogen atoms, which might point to its being H_2SO_4. The action of SO_2 on PbO_2 or MnO_2 results in the formation of $PbSO_4$, or $MnSO_4$, a similar case to the first example. The action again of dry H_2SO_4

on NaCl, whereby $NaHSO_4$ and HCl are formed, points to the constitution $H.SO_3.OH$. The electrolytic decomposition *may* point to H_2SO_4 but the action is probably very complex.

Several compounds of oxides of sulphur with chlorine, with oxides of nitrogen, or even with HCl, are known, and their method of formation points to the existence of the group HO in the acids of sulphur, and also in most, if not all, other so-called oxy-acids or negative hydrates like nitric or phosphoric acid. The action of PCl_5 and $POCl_3$ on some of these acids, as H_2SO_4, also, by analogy with the actions of these reagents on alcoholic and similar bodies, points to the existence of HO in combination.

The compounds PCl_3, PCl_5, and $POCl_3$ act on water thus:

$$PCl_3 + H_2O = POCl + 2HCl; \quad PCl_5 + H_2O = POCl_3 + 2HCl, \ \&c.$$

On alcohol, C_2H_5OH thus:

$$PCl_5 + C_2H_5OH = POCl_3 + HCl + C_2H_5Cl.$$

Also on acetic acid,

$$CH_3COOH + PCl_5 = POCl_3 + HCl + CH_3COCl.$$

Also $POCl_3$ on sulphuric acid,

$$2SO_2{}^{OH}_{OH} + POCl_3 = 2SO_2{}^{Cl}_{OH} + HCl + HPO_3.$$

It will be seen from this that great difficulties exist in ascertaining the real structure of mineral compounds as yet; but it does no harm whatever to form a mental picture of the possible structure of these bodies, keeping as close to experimental facts as possible.

The following table is therefore arranged so that from the probable constitution of the acid that of the salt may be expressed.

The metallic bases are distinguished as *monad*, *dyad*, *triad*, *tetrad*, *pentad*, and *hexad*, the acid representing the monad combination being in the first column.

Other metals are represented by M'', M''', M^{iv}, M^{v}, M^{vi}. In addition to the normal salts, various other constitutional formulæ of mixed and basic compounds are given. The basicity of the acid is placed in brackets after its empirical formula.

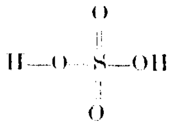
Acid.	Structural formula.	Dyad salts.	Triad salts.	Tetrad salts.	Pentad salts.	Hexad salts.
			Nitric Acid.			
HNO_3 (1)	NO_2HO	$\begin{cases} NO_2M''O_2 \\ NO_2 \end{cases}$ or $N_2O_4M''O_2$	$\begin{rcases} NO_2 \\ NO_2M'''O_3 \\ NO_2 \end{rcases}$ or $N_3O_6M'''O_3$	$(NO_2)_4M^{iv}O_4$	$(NO_2)_5M^{v}O_5$	$(NO_2)_6M^{vi}O_6$.
Ferric nitrate (pseudo-triad), $Fe_2N_6O_{18} = (NO_2)_6Fe_2O_6$. Mercurous nitrate, $Hg_2N_2O_6 = (NO_2)_2Hg_2O_2$.						
			Nitrous Acid.			
Normal nitrites are written as nitrates, but the group (NO) is substituted for (NO_2).						
			Carbonic Acid.			
H_2CO_3 (2)	$CO(HO)_2$	$COM''O_2$	$(CO)_3(M'''O_3)_2$	$(CO)_2M^{iv}O_4$	$(CO)_5(M^{v}O_5)_2$	$(CO)_6M^{vi}O_6$.
			Sulphuric Acid.			
H_2SO_4 (2)	$SO_2(HO)_2$	$SO_2M''O_2$	$(SO_2)_3(M'''O_3)_2$	$(SO_2)_2M^{iv}O_4$	$(SO_2)_5(M^{v}O_5)_2$	$(SO_2)_6M^{vi}O_6$.
			Sulphurous Acid, $SO(HO)_2$.			
Normal sulphites are written as sulphates, but the group (SO) is substituted for (SO_2).						
			Phosphoric Acid.			
H_3PO_4 (3)	$PO(HO)_3$	$(PO)_2(M''O_2)_3$	$(PO)_3M'''O_3$	$(PO)_4(M^{iv}O_4)_3$	$(PO)_5(M^{v}O_5)_3$	$(PO)_2M^{vi}O_6$.
			Silicic Acid (Ortho).			
H_4SiO_4 (4)	$Si(HO)_4$	$Si(M''O_2)_2$	$Si_3(M'''O_3)_4$	$Si(M^{iv}O)_4$	$Si_5(M^{v}O_5)_4$	$Si_3(M^{vi}O_6)_2$.

From the above examples in which the structural formulæ of mono-, di-, tri- and tetra-basic acids are given, it will be found easy to deduce general rules for making structural formulæ for all sorts, especially if the relative proportion of the metal to the negative element is carefully noticed.

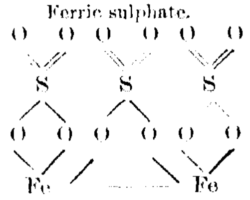
The examples are given only in the case of normal salts; but it will be found simple, if they are well remembered, to construct constitutional formulæ for any acid or basic salt, and from these graphic formulæ:

Examples of Graphic Formulæ.

H_2SO_4 =



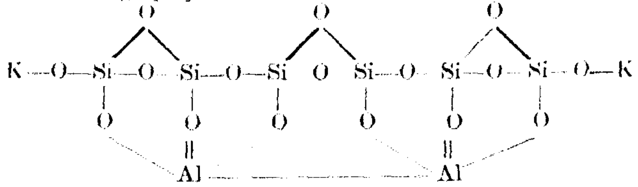
Ferric sulphate.



H_4SiO_4.

Felspar.

$Si_6O_{16}K_2Al_2$ =



See also in the text the nucleus group formulæ proposed for some double salts as the chloroplatinates and others.

Many points in this connection are waiting for further investigation.

See, in this connection, papers on constitutional formulæ of inorganic compounds in the "Zeitschrift für unorganische chemie" during the year 1897.

APPENDIX VI.

It is most particularly recommended that all reagents be made up for the use of students as equivalent solutions. There is no difficulty whatever in carrying this out, and the advantage in practical teaching is very great. *Approximately equal volumes* of reagent solutions will then react completely, or neutralise each other.

The tendency is generally to take too much for an analysis, and be in consequence working with very concentrated solutions and precipitates it is difficult to wash properly. An equivalent reagent solution will be found to help most speedily in correcting this.

These remarks appeared in a previous edition. Extended trial has further proved their advantages over the ordinary uncertain, indeed unknown, solutions. An additional table is given after this one, slightly modified from Mr. Reddrop's paper in the *Chemical News* (No. 1591).

REAGENTS.

SOLVENTS.

Distilled Water.*—Obtained by condensing steam by means of a tin worm. The first portions of the condensed water usually contain carbonic anhydride and ammonium carbonate, and should be rejected.

Impurities.—When evaporated in a platinum vessel, distilled water should not leave a solid residue, either organic or mineral. Ammonium sulphide ought not to give a precipitate (Cu, Pb, Fe), neither ought basic lead acetate to cause a turbidity (CO_2, $(NH_4)_2CO_3$). No turbidity or precipitate should be produced on the addition of ammonium oxalate (lime), barium chloride (sulphates), or silver nitrate (chlorides). Pure distilled water is colourless, inodorous, and tasteless.

Water used for Nessler's test should be specially distilled in a glass retort with a few pieces of caustic potash and a little permanganate of potash, and the distillate rejected as long as the Nessler solution indicates any traces of ammonia.

Alcohol (Methylated Spirit), C_2H_6HO or EtHO.—Ordinary methylated spirit (*i.e.*, ethylic alcohol, 90 per cent.), may be employed

* The asterisk marks the more important reagents.

for most purposes. It can be rendered practically absolute by shaking with well-dried potassium carbonate, and distilling the clear spirit in a flask or retort from a water-bath.

Impurities.—Commercial methylated spirit frequently leaves a residue on evaporation; if so, it should be rectified by distillation. It should be without action on litmus papers.

Ether.—Ordinary ether (methylated, *i.e.*, prepared from methylated alcohol) of commerce is pure enough. It should have some dried K_2CO_3 in the bottle.

ACIDS.

Sulphuric Acid,* H_2SO_4.—Common oil of vitriol may be used in all operations with which its usual impurities (lead, arsenic, iron, lime, nitric acid) do not interfere. Sulphuric acid, free from arsenic, should be employed for generating arsenious or antimonious hydride, and an acid free from lead, whenever this metal has to be precipitated as sulphate. Sulphuric acid, free from nitric acid and nitric peroxide, must be employed in testing for nitric acid by means of ferrous sulphate.

Impurities.—Pure sulphuric acid is colourless, and leaves no residue on evaporation in a porcelain dish. When a solution of ferrous sulphate is poured upon it in a narrow test-tube, it should not form a brown ring where the two liquids come in contact (nitric acid and nitric peroxide), nor strike a blue colour when a highly diluted solution of the acid is added to a solution of pure potassium iodide and starch paste (nitrous acid). The presence of arsenic is best ascertained by passing a current of sulphuretted hydrogen through the dilute acid, or by generating hydrogen from zinc free from arsenic, and passing the gas through an ignited combustion-tube (Marsh's test, Fig. 14). Lead sulphate is frequently found in sulphuric acid, and is precipitated on diluting with water, being less soluble in dilute than in concentrated acid. Hydrochloric acid should cause no turbidity (lead) where the two liquids meet.

The pure acid can readily be bought, and the student need not attempt to purify the crude acid.

Dilute Sulphuric Acid.*—Prepare by pouring slowly one part by measure of the concentrated acid (sp. gr. 1·8) into five parts by measure of distilled water, with continuous stirring. Thin glass vessels (beakers), or a porcelain dish, should be employed, as much heat is evolved. Allowed the lead sulphate to subside, and decant or syphon off the clear liquid.

Nitric Acid (Aqua Fortis) HNO_3.—Should be colourless, and leave no residue on evaporation in a glass dish.

Impurities.—Sulphuric and hydrochloric acid. Dilute considerably, and test portions with baric nitrate and silver nitrate.

Dilute Nitric Acid.*—Prepared by diluting one part of pure

commercial acid (sp. gr. 1·38 to 1·45), with three parts of distilled water.

CRUDE NITRIC ACID.*—May be employed for all experiments in which the above impurities do not interfere, *e.g.*, in the preparation of N_2O_2 or N_2O_3 by the action of nitric acid upon copper or arsenious anhydride.

CONCENTRATED HYDROCHLORIC ACID,* MURIATIC ACID, HCl. Should be colourless, and leave no residue on evaporation.

Impurities.—Ferric chloride, sulphurous and sulphuric acids, arsenic. The dilute acid should not impart a blue colour to a solution of KI and starch paste (Cl or Fe_2Cl_6).—On adding a few drops of a solution containing iodide of starch, the blue colour should not be destroyed (SO_2). The dilute acid should remain clear on the addition of a solution of barium chloride (H_2SO_4). Sulphuretted hydrogen, when passed through the dilute acid should not produce a precipitate (arsenic), nor should ammonium sulphocyanate redden the diluted acid (iron).

CRUDE HYDROCHLORIC ACID.*—Should be employed whenever the impurities which it contains do not interfere with the object in view, as, for instance, in the preparation of chlorine from manganic dioxide.

AQUA REGIA OR NITROHYDROCHLORIC ACID.—Prepared, when required *only*, by mixing one part of concentrated nitric acid with three to four parts of hydrochloric acid.

SULPHUROUS ACID, H_2SO_3.—Prepared by acting with concentrated sulphuric acid upon copper, and passing the gas into water. The solution should be kept in a well-stoppered bottle.

CARBONIC ACID WATER.—A solution is prepared by acting with hydrocholoric acid upon marble, and passing the evolved carbonic anhydride into water.

CHLORINE WATER.—A solution of chlorine in water is readily prepared. It should be kept in a well-stoppered bottle, and in a dark place, since on exposure to light, it is speedily converted into HCl with evolution of oxygen.

ACETIC ACID.* $\begin{cases} CH_3 \\ COOH. \end{cases}$ It should leave no residue on evaporation.

Impurities.—Sulphuric and hydrochloric acids, lead, copper, iron, lime.

TARTARIC ACID, $C_4H_6O_6 = \overline{T}(HO)_2$.—A solution is prepared when required only, as the acid undergoes decomposition in an aqueous solution.

Impurities.—Tartaric acid contains sometimes gypsum and calcium tartrate, which are best tested for by igniting a few crystals

on platinum, extracting the residue, if any, with a few drops of dilute HCl, and adding to one portion $BaCl_2$, to another ammonia and ammonium oxalate.

Oxalic Acid, $H_2C_2O_4$. The commercial acid is sufficiently pure. It should not leave more than a trace of a residue on ignition.

Impurities.—Iron, potassium and sodium oxalates, lime.

Hydrofluoric Acid, HF.—A solution stored up in a gutta-percha bottle is best bought, as its preparation involves expensive apparatus. It should leave no fixed residue on evaporation to dryness.

Hydrofluosilicic Acid, $2HF,SiF_4$.—A solution of this acid in water is prepared as described under silicates, &c. It should be made sufficiently strong to precipitate a soluble barium salt readily.

Impurities.—Owing to the mode of preparation the acid is often contaminated with sulphuric acid. It should not produce a precipitate in a solution of a strontium salt.

Hydrosulphuric Acid, SH_2.—Prepared when required. In well-appointed laboratories sulphuretted hydrogen is now usually stored in a gasholder over oil, and supplied like coal gas from small taps, in closets, connected with the chimney. The gas, whether obtained from a constant generating apparatus, or from a gas-holder, should invariably be passed through a wash-bottle containing water. A saturated solution of sulphuretted hydrogen in water answers most purposes of the analyst. It should be kept in a well-stoppered bottle, since sulphuretted hydrogen decomposes rapidly when in contact with air with formation of sulphur acids and precipitation of white sulphur.

If the gas be required entirely free from AsH_3, it should be generated by acting with pure HCl (concentrated) upon native *grey antimony*, Sb_2S_3.

BASES AND METALS.

Potassium Hydrate,* KHO, or Sodium Hydrate, NaHO.—Usually obtained in commerce in the form of sticks or lumps.

Impurities.—Silica, alumina, phosphoric, sulphuric, and hydrochloric acids (sulphates and chlorides, often in not inconsiderable quantities), and carbonic acid. On dissolving in water, and allowing the suspended matter to subside, the clear solution may be syphoned off.

Pure sodium hydrate is indispensable for the separation of alumina from the oxides of iron and chromium.

Ammonium Hydrate,* NH_4OH.—The *liquor ammonii caustici* of commerce has a sp. gr. ·88.

Impurities.—A solution of ammonia should be colourless; on

neutralising with pure HCl it should remain inodorous. When evaporated in a glass or platinum dish, it should not leave any residue. Ammonia frequently contains traces of sulphuric and hydrochloric acids, and sometimes not inconsiderable quantities of ammonium carbonate, when it will produce a white precipitate on the addition of lime-water, and sometimes other bases.

BARIUM HYDRATE,* $Ba(HO)_2$).

Impurities.—The solution, commonly called baryta-water, should, on precipitating with pure H_2SO_4, give a filtrate which leaves no fixed residue on evaporating to dryness in a platinum vessel.

CALCIUM HYDRATE,* $Ca(HO)_2$.—Freshly slaked lime in powder is used in qualitative analysis, as well as a solution of lime, so called lime-water. This is prepared by dissolving in cold distilled water some freshly slaked lime, allowing to subside in a stoppered bottle, and syphoning off the clear liquid into another bottle.

AMMONIUM SULPHIDE,* $(NH_4)_2S$.—Prepared by saturating three parts of ammonic hydrate with sulphuretted hydrogen gas, whereby $SHNH_4$ is formed. On diluting this solution of hydrogen ammonium sulphide with two parts of ammonium hydrate, a sulphide is obtained which contains a little free ammonia. The concentrated solution may be diluted with ten times its bulk of water. It should be kept in well-stoppered bottles. Calcium or magnesium salts should not be precipitated; nor should the solution leave a residue on evaporation and ignition. The oxygen of the air decomposes it gradually into NH_3, OH_2, and yellow ammonium sulphide $= (NH_4)_2S_n$.

YELLOW AMMONIUM SULPHIDE.—Used for the solution and conversion of SnS into SnS_2. It may be prepared by digesting the neutral $(NH_4)_2S$ with flowers of sulphur, and filtering the liquid.

SODIUM SULPHIDE, SNa_2.—Prepared by saturating one portion of a solution of sodium hydrate with sulphuretted hydrogen, and adding it to the second portion. A little ferrous sulphide, which is generally precipitated, is filtered off. The solution must be kept in a well-stoppered bottle.

SODA-LIME AND CHARCOAL.—This is a most useful reagent for ammonia, mercury, arsenic, cadmium, in the dry way: Mix two parts CaO with one part NaHO and one of charcoal, moisten with water and mix thoroughly into a paste; place in a covered clay crucible, and dry thoroughly in an oven; pound up, and keep closely corked up.

SALTS.

HYDROGEN DISODIUM PHOSPHATE,* $HNa_2PO_4 + 12$ Aq.—Recrystallise the commercial salt.

Impurities.—Sulphate and chloride. Ammonium hydrate should not cause any turbidity on warming (alkaline earthy phosphates).

SODIUM ACETATE $\left\{\begin{matrix} CH_3 \\ CONa \end{matrix}\right.$ + 6 Aq. The commercial salt generally contains sodium sulphate. If a pure salt cannot be procured, sodium acetate may be prepared by neutralising pure sodium carbonate with pure acetic acid.

SODIUM HYPOCHLORITE, ClNaO.—Prepared by shaking up one part of bleaching powder with ten parts of water, and adding a saturated solution of commercial sodic carbonate as long as a precipitate is produced. Allow to subside, and syphon off.

AMMONIUM OXALATE.*—Purify the commercial salt by recrystallisation.

Impurities.—The salt should leave no fixed residue on ignition. Sulphuretted hydrogen or ammonium sulphide ought not to produce a turbidity or a precipitate.

AMMONIUM CARBONATE.*

Impurities.—Iron, lead, sulphuric and hydrochloric acids. The salt should volatilise completely, and give no precipitate with barium chloride or silver nitrate (after acidulating with hydrochloric or nitric acid respectively), also no precipitate with sulphuretted hydrogen or ammonium sulphide.

HYDROGEN AMMONIUM CARBONATE, NH_4HCO_3.—Obtained in colourless rhombic prisms, on passing carbonic anhydride to supersaturation into a concentrated solution of ammonia. The salt is employed for the separation of As_2S_3 from Sb_2S_3 and SnS_2. A saturated solution is prepared when required.

AMMONIUM CHLORIDE.*—The commercial salt (sal-ammoniac) usually contains iron. Purify by adding to the solution a little ammonium hydrate. Allow the ferric hydrate to subside, and neutralise the alkaline filtrate exactly with pure HCl. The salt should leave no fixed residue on ignition.

AMMONIUM MOLYBDATE.—This salt may be purchased. It is dissolved in strong ammonia and allowed to stand for some time. A slight yellow precipitate containing ferric hydrate, usually subsides. The clear fluid is poured into concentrated nitric acid as long as the molybdic acid which at first precipitates is entirely redissolved. The nitric acid solution should remain colourless on boiling. A yellow precipitate indicates contamination with phosphoric acid, and the reagent should not be used till it remains clear on digestion.

AMMONIUM SULPHATE.—Recrystallise the commercial salt from an ammoniacal solution in order to separate iron. Keep a saturated solution for use.

AMMONIUM NITRATE, NH_4NO_3.—The commercial salt is dissolved, when required, to a saturated solution. It should leave no residue when ignited on platinum.

BARIUM CHLORIDE,* $BaCl_2 + 2$ Aq.—The commercial salt is rarely pure enough, and not infrequently contains lead. It should not give a precipitate with sulphuretted hydrogen or ammonium sulphide, nor should a residue be left after precipitating the whole of the barium by pure sulphuric acid and evaporating the filtrate in a platinum dish. Purify, if necessary, by passing a current of sulphuretted hydrogen, filtering, and recrystallising.

BARIUM NITRATE, $Ba(NO_3)_2$.—Should not be precipitated by silver nitrate, as it is sometimes employed, instead of barium chloride, in order to avoid introducing any chlorine into a solution. Pure barium acetate answers the same purpose. For other impurities, test as for barium chloride.

BARIUM CARBONATE, $BaCO_3$.—Prepared by precipitation of pure barium chloride with ammonium carbonate and ammonia. Wash well till free from NH_4Cl, stir up the precipitated barium carbonate with water to a thick creamy consistency, and keep it for use in a stoppered bottle. Shake up before using this reagent.

CALCIUM CHLORIDE,* $CaCl_2 + 6$ Aq.—The solution should be neutral to test-papers, and should not be precipitated by ammonium sulphide (iron).

CALCIUM SULPHATE, $CaSO_4$.—A saturated solution is prepared by repeatedly shaking up gypsum with water, allowing to subside, and syphoning off the clear liquid.

MAGNESIUM SULPHATE.—The commercial salt ($MgSO_4OH_2$ + 6 Aq.). Recrystallise.

FERROUS SULPHATE.—The commercial salt, $FeSO_4 + 7OH_2$, is pure enough.

FERRIC CHLORIDE,* Fe_2Cl_6.—Prepared by dissolving freshly precipitated and well washed $Fe_2(HO)_6$ in pure HCl, keeping the ferric hydrate in excess.

SILVER NITRATE,* $AgNO_3$.—Prepared either from silver (pure), or from a silver alloy (a silver coin), by dissolving in pure nitric acid, and precipitation as AgCl. Filter off the copper salt, and wash thoroughly with hot water; transfer to a porcelain dish, and introduce clean strips of zinc. Collect the finely divided silver on a filter, wash thoroughly with hot water acidulated with a little sulphuric acid, and dissolve in dilute nitric acid. Evaporate the solution to dryness, and fuse the residue gently.

NESSLER'S SOLUTION.—Dissolve 3·5 grms. of KI in 10 cc. of water; next dissolve 1·6 grm. of $HgCl_2$ in 30 cc. of water; add the mercury solution gradually and with continuous agitation to the solution of potassium iodide, until the precipitate ceases to be redissolved; then add 60 cc. of potassium hydrate and filter. Keep in a small bottle, out of contact with ammonia fumes.

This reagent is of great value for the detection of mere traces of ammonia.

CUPRIC SULPHATE.—The commercial salt ($CuSO_4$ + 5 Aq.) is purified by repeated crystallisation.

Impurities.—Iron, zinc.

CUPROUS CHLORIDE, Cu'_2Cl_2.—Obtained by digesting $CuCl_2$ with metallic copper and HCl.

STANNOUS CHLORIDE, $SnCl_2$.—Prepared by boiling pure granulated tin in concentrated HCl, with the aid of a piece of platinum foil. Keep the filtered solution over granulated tin in a small stoppered bottle. It is best made as wanted in a test-tube.

AURIC CHLORIDE, $AuCl_3$.—Prepared by dissolving pure gold in aqua regia, evaporating to dryness on a water-bath and dissolving in water.

PLATINIC CHLORIDE, $PtCl_4$.—Dissolve some platinum scraps in aqua regia. Precipitate with NH_4Cl. Collect precipitate on a Swedish filter-paper; wash with strong alcohol; dry and ignite in a porcelain crucible, gently at first, and lastly to intense redness. Redissolve the spongy platinum in aqua regia. Evaporate repeatedly to dryness on a water-bath, with addition of HCl. Pure platinic chloride should dissolve completely in pure alcohol.

Zinc, free from arsenic, granulated, and in the form of strips or sticks.

Iron (steel), Copper, Tin, Lead, Platinum (used in the form of wire, bars, sheets, turnings) and Mercury can be obtained of sufficient purity for the purposes of qualitative analysis.

METALLIC LEAD FREE FROM SILVER.—Prepared by precipitation of lead acetate by metallic zinc, washing with hot water, then alcohol and melting in a dry crucible.

PLUMBIC DIOXIDE, PbO_2.—Readily prepared by digesting red lead in boiling dilute nitric acid. The brown powder is well washed by decantation, and lastly on the filter.

MANGANIC DIOXIDE, MnO_2.—Use the powdered commercial black oxide.

HYDROGEN PEROXIDE, O_2H_2, or $(HO)_2$.—A solution may be prepared by passing a current of carbonic anhydride through water in which barium peroxide is suspended. The precipitated barium

carbonate is filtered off. The commercial article usually contains a little free mineral acid, such as HCl or H_2SO_4, added in order to prevent its spontaneous decomposition. Hydrofluosilicic acid is also sometimes met with, used probably (in excess) to remove any soluble barium salt.

Reagents used for Fusions and for Blowpipe Reactions.

Sodium Carbonate,* Na_2CO_3.—Should be free from sulphate and chloride.

Fusion Mixture,* or White Flux.—Consisting of dry Na_2CO_3 and K_2CO_3, mixed in the proportion of their combining weights, *i.e.*, 106 + 138, or in the proportion of 10 to 13.

Pure carbonates free from silica, chlorides, and sulphates, should be procured, as their purification cannot be effected without using silver and platinum vessels.

Black Flux.—Prepared by igniting crystals of Rochelle salt (potassio-sodium tartrate) in a platinum or iron crucible. The residue consists of carbon and alkaline carbonates.

Microcosmic Salt,* NH_4NaPO_4 + 8 Aq.—The salt should be dried, and used in the form of a powder. On being heated in a loop of platinum wire it is converted into $NaPO_3$.

Potassium Cyanide,* KCy.—Exceedingly useful for reducing metallic oxides and sulphides, either in the crucible or on charcoal. For blowpipe reactions a mixture of equal parts of KCy and Na_2CO_3, (or fusion mixture) is preferable, because it sinks readily into the charcoal, and yields metallic globules of great purity. For the separation of Ni and Co the salt is dissolved, when required, in twenty parts of cold water, as its aqueous solution is rapidly decomposed.

Potassium Nitrate,* KNO_3.—Used as an oxidising agent. The commerical salt should be purified by dissolving the crystals in hot water to a saturated solution, and allowing to cool in a porcelain dish with continuous stirring. The nitrate falls out first as a fine white powder, "meal nitre," and the impurities—*e.g.*, phosphate, sulphate, or chloride—are left in the mother-liquor.

Potassium Chlorate,* $\left\{\begin{matrix} OCl \\ OKO \end{matrix}\right.$.—This salt can readily be obtained pure—*i.e.*, free from chloride. Either by itself, or in conjunction with hydrochloric acid, it serves as a powerful oxidising agent.

Borax,* $B_4O_5(NaO)_2$ or $Na_2B_4O_7$ + 10 Aq.—The crystals should be gently heated in a platinum crucible till the water of crystallisation has been driven off, and the mass kept powdered and ready for use in blowpipe reactions.

Hydrogen Potassium Sulphate, $KHSO_4$.—Prepared by heating in a platinum dish 87 parts of normal potassium sulphate with 49 parts of pure sulphuric acid, till the clear mass fuses steadily. Pour out on a porcelain slab, and keep the lumps in a bottle.

Cobaltous Nitrate, $Co(NO_3)_2$.—Used in solution only. Should be free from other metals. It is best to dissolve the nitrate in hot water, saturate with ammonia, and either expose to air or add a few drops of H_2O_2. After it has formed a brown solution, filter, and neutralise with nitric acid.

Vegetable Colouring Matters—Test-papers.

Litmus Solution.—Digest the small pieces of commercial litmus with pure water until a strong purple-blue solution is formed, and filter. It should be diluted so that one drop of reagent—diluted HCl—added to half a pint, will turn it red, and a similar quantity of NH_4OH turn it blue. Litmus-paper is made by immersing filter-paper in above solutions, and drying out of contact with acid or ammonia fumes.

Turmeric Paper.—Prepared by digesting at a gentle heat one part of turmeric root with six parts of alcohol. Filter and soak strips of porous paper with the yellow extract. The dried papers should exhibit a fine yellow tint. Like litmus-papers, they serve for the detection of free alkalies. All test-papers should be kept in well-stoppered bottles or wooden boxes.

Indigo Solution.—Prepared by gradually stirring four to six parts of fuming sulphuric acid into one part of finely divided indigo, and allowing the mixture to stand for 48 hours before pouring into it 20 parts of water. Filter, and keep for use in a dark place. The solution of indigo is used for detecting nitric acid, chloric acid, and free chlorine, owing to the formation of products of oxidation of a yellow colour.

A considerable number of organic substances have been proposed as colour reagents in the same sense as litmus; that is, for distinguishing the point where acidity ends or where alkalinity begins. Some of these are mentioned in the Appendix on Volumetric Analysis.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight.	Equivalent System. Grms. per litre.	Equivalent System. Strength.
Sulphuric Acid	H_2SO_4	98	49	—	36 N
,,	,,	,,	,,	—	5 N
,,	,,	,,	,,	49	N
Nitric Acid	HNO_3	63	63	—	24 N
,,	,,	,,	,,	—	16 N
,,	,,	,,	,,	—	5 N
,,	,,	,,	,,	63	N
Hydrochloric Acid	HCl	36·5	36·5	—	10 N
,,	,,	,,	,,	—	5 N
,,	,,	,,	,,	36·5	N
Sulphurous Acid	H_2SO_3	82	41	—	4 N
Carbonic Acid	H_2CO_3	62	31	—	$\frac{N}{10}$
Acetic Acid	$HC_2H_3O_2$	60	60	—	17 N
,,	,,	,,	,,	—	5 N
,,	,,	,,	,,	60	N
Tartaric Acid	$H_2C_4H_4O_6$	150	75	—	5 N
,,	,,	,,	,,	75	N
Citric Acid	$H_3C_6H_5O_7$	192	64	—	5 N
,,	,,	,,	,,	64	N
Oxalic Acid	$H_2C_2O_4$	90	45	—	$\frac{3 N}{2}$
Hydrofluoric Acid	HF	20	20	—	12 N ?
Hydrofluosilicic Acid	H_2SiF_6	144	72	—	—
,,	,,	,,	,,	—	N
Hydrogen Sulphide	H_2S	34	17	—	$\frac{N}{4}$
Chlorine Water	Cl_2	71	35·5	—	$\frac{N}{5}$
Bromine	Br_2	160	80	—	37 N
Bromine Water	,,	,,	,,	—	$\frac{N}{2}$
Hydrogen Peroxide	H_2O_2	34	17	—	4 N
,,	,,	,,	,,	—	2 N
Potassium Hydrate	KHO	56	56	—	5 N
,,	,,	,,	,,	56	N
Sodium Hydrate	NaHO	40	40	—	5 N
,,	,,	,,	,,	40	N
Ammonium Hydrate	NH_4OH	35	35	—	20 N
,,	,,	,,	,,	—	5 N
,,	,,	,,	,,	35	N
Barium Oxide	BaO	153	76·5	—	$\frac{N}{3}$
Calcium Oxide	CaO	56	28	—	$\frac{N}{20}$
Ammonium Sulphide	$(NH_4)_2S$	68	34	—	5 N
,,	,,	,,	,,	34	N

Symbol of Substance taken.	Method of Preparing Reagent.
—	Sulphuric acid, sp. gr. 1·8427 at 15·5° C.
—	Sulphuric acid diluted to sp. gr. 1·1527 at 15·5°.
—	200 cc. of 5 N sulphuric acid diluted to 1 litre.
—	Nitric acid sp. gr. 1·50.
—	Nitric acid sp. gr. 1·4268 at 15·5° C.
—	Nitric acid diluted to sp. gr. 1·1656 at 15·5° C.
—	280 cc. of 5 N nitric acid diluted to 1 litre.
—	Hydrochloric acid sp. gr. 1·1611 at 15·5° C.
—	Hydrochloric acid diluted to sp. gr. 1·0843 at 15·5° C.
—	200 cc. of 5 N hydrochloric acid diluted to 1 litre.
—	Water at 15·5° C. saturated with sulphur dioxide (sp. gr. 1·052).
—	Water at 15·5° C. saturated with carbon dioxide.
—	Acetic acid solid at 10° C.
—	294 cc. of 17 N acetic acid diluted to 1 litre.
—	200 cc. of 5 N acetic acid diluted to 1 litre.
$H_2C_4H_4O_6$	375 grm. dissolved and diluted to 1 litre.
"	75 " " "
$H_3C_6H_5O_7,Aq$	350 " " "
"	70 " " "
$H_2C_2O_4,2Aq$	94·5 " " "
—	Hydrofluoric acid, sp. gr. 1·15 ?
—	Water at 15·5° C. saturated with hydrogen sulphide.
—	Water at 15·5° C. saturated with chlorine.
—	Pure liquid bromine.
—	Water at 15·5° C. saturated with bromine.
—	Hydrogen peroxide, 20 volume solution.
—	" " 10 " "
KHO	280 grms. dissolved and diluted to 1 litre.
"	56 " " "
NaHO	200 " " "
"	40 " " "
—	Ammonium hydrate sp. gr. 0·880.
—	Ammonium hydrate diluted to sp. gr. 0·9643 at 15·5°
—	200 cc. of 5 N ammonium hydrate diluted to 1 litre.
$BaH_2O_2,8Aq$	52·5 grm. dissolved and diluted to 1 litre.
—	Water at 15·5° C. saturated with calcium hydrate.
—	Saturate 600 cc. of 5 N ammonium hydrate with H_2S in a corked flask, and then add 400 cc. of 5 N ammonium hydrate.
—	200 cc. of 5 N ammonium sulphide diluted to 1 litre.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight.	Equivalent System.	
				Grms. per litre.	Strength.
Sodium Sulphide	Na_2S	78	39	—	5 N
"	"	"	"	39	N
Potassium Cyanide	KCy	65	65	65	N
Potassium Sulphate	K_2SO_4	174	87	87	N
Potassium Iodide	KI	166	166	166	N
"	"	"	"	—	$\frac{N}{5}$
Potassium Chromate	K_2CrO_4	194·5	97·25	97·25	N
Potassium Metantimoniate	$KSbO_3$	209	209	3·07	$\frac{N}{68}$
Potassium Ferrocyanide	K_4FeCy_6	368	92	92	N
Potassium Ferricyanide	$K_6Fe_2Cy_{12}$	658	109·7	109·7	N
Potassium Sulphocyanate	KCyS	97	97	97	N
Sodium Carbonate	Na_2CO_3	106	53	—	3 N
"	"	"	"	53	N
Hydrogen Disodium Phosphate	HNa_2PO_4	142	47·3	47·3	$\frac{2N}{3}$ or N
Sodium Acetate	$NaC_2H_3O_2$	82	82	—	4 N
Sodium Sulphite	Na_2SO_3	126	63	—	2 N
Sodium Thiosulphate	$Na_2S_2O_3$	158	79	79	$\frac{N}{2}$ or N
Sodium Hypochlorite	NaClO	74·5	74·5	—	—
Ammonium Acetate	$NH_4C_2H_3O_2$	77	77	—	5 N
"	"	"	"	77	N
Ammonium Oxalate	$(NH_4)_2C_2O_4$	124	62	37·2	$\frac{3N}{5}$
Hydrogen Di-ammonium Phosphate	$H(NH_4)_2PO_4$	132	44	44	$\frac{2N}{3}$ or N
Ammonium Carbonate	$(NH_4)_2CO_3$	96	48	—	5 N
"	"	"	"	48	N
Hydrogen Ammonium Carbonate	$H(NH_4)CO_3$	79		—	$\frac{3N}{2}$ or 3 N
Ammonium Chloride	NH_4Cl	53·5	53·5	—	5 N
"	"	"	"	53·5	N
Ammonium Sulphate	$(NH_4)_2SO_4$	132	66	66	N
Barium Chloride	$BaCl_2$	208	104	104	N
Barium Nitrate	BaN_2O_6	261	130·5	65·25	$\frac{N}{2}$
Barium Carbonate	$BaCO_3$	197	98·5	—	2 N
Strontium Sulphate	$SrSO_4$	183·5	91·75	0·153	$\frac{N}{600}$
Calcium Chloride	$CaCl_2$	111	55·5	55·5	N

Symbol of *Substance* taken.	*Method of Preparing Reagent.*
—	Dissolve 200 grms. of sodium hydrate in 800 cc. water, saturate one-half with H_2S, then add the other half and dilute to 1 litre.
—	200 cc. of 5 N sodium sulphide diluted to 1 litre.
KCy	65 grms. crystals dissolved and diluted to 1 litre.
K_2SO_4	87 grms. dissolved and diluted to 1 litre.
KI	166 ,, ,, ,,
,,	33·2 ,, ,, ,,
K_2CrO_4	97·25 ,, ,, ,,
$K_2Sb_2O_6,7Aq$	Saturated solution at 15·5 C.
$K_4FeCy_6,3Aq$	105·5 grm. dissolved and diluted to 1 litre.
$K_6Fe_2Cy_{12}$	109·7 ,, ,, ,,
$KCyS$	97 ,, ,, ,,
$Na_2CO_3,10Aq$	429 grms. dissolved and diluted to 1 litre.
,,	143 ,, ,, ,,
$HNa_2PO_4,12Aq$	119·3 ,, ,, ,,
$NaC_2H_3O_2,3Aq$	544 ,, ,, ,,
$Na_2SO_3,7Aq$	252 ,, ,, ,,
$Na_2S_2O_3,5Aq$	124 ,, ,, ,,
—	
—	294 cc. of 17 N acetic acid, neutralised with strong ammonium hydrate and diluted to 1 litre.
—	200 cc. of 5 N ammonium acetate diluted to 1 litre.
$C_2O_4(NH_4)_2$	42·6 grms. dissolved and diluted to 1 litre.
$H(NH_4)_2PO_4$	44 grms. dissolved and diluted to 1 litre.
—	196·7 grms. of ammonium sesquicarbonate dissolved in 333·3 cc. of 5 N ammonium hydrate and diluted to 1 litre.
—	200 cc. of 5 N ammonium carbonate solution diluted to 1 litre.
—	A saturated solution made by passing excess of carbon dioxide into 3 N ammonium hydrate.
NH_4Cl	267·5 grms. dissolved and diluted to 1 litre.
,,	53·5 ,, ,, ,,
$(NH_4)_2SO_4$	66 ,, ,, ,,
$BaCl_2,2Aq$	122 ,, ,, ,,
BaN_2O_6	65·25 ,, ,, ,,
$BaCO_3$	197 grms., freshly precipitated, suspended in water and diluted to 1 litre.
$SrSO_4$	Water at 15·5° C. saturated with precipitated strontium sulphate.
$CaCl_2,6Aq$	109·5 grms. dissolved and diluted to 1 litre.

Name of Reagent.	Symbol.	Molecular weight.	Equivalent weight.	Equivalent System.	
				Grms. per litre.	Strength.
Calcium Sulphate . .	$CaSO_4$	136	68	2·27	$\frac{N}{30}$
Magnesium Chloride .	$MgCl_2$	95	47·5	47·5	N
Magnesium Sulphate .	$MgSO_4$	120	60	60	N
Ferrous Sulphate . .	$FeSO_4$	152	76	76	N
Ferric Chloride . .	Fe_2Cl_6	325	54·17	54·17	N
Plumbic Acetate . .	$PbC_4H_6O_4$	325	162·5	162·5	N
Plumbic Nitrate . .	PbN_2O_6	331	165·5	165·5	N
Argentic Nitrate . .	$AgNO_3$	170	170	170	N
"	"	"	"	—	$\frac{N}{5}$
Argentic Sulphate . .	Ag_2SO_4	312	156	7·8	$\frac{N}{20}$
Mercurous Nitrate . .	$Hg_2N_2O_6$	524	262	52·4 +	$\frac{N}{5}$ +
Mercuric Chloride . .	$HgCl_2$	271	135·5	54·2	$\frac{2\,N}{5}$
Cupric Sulphate . .	$CuSO_4$	159·5	79·75	79·75	N
Cupric Chloride . .	$CuCl_2$	134·5	67·25	67·25	N
Stannous Chloride . .	$SnCl_2$	189	94·5	94·5 +	N +
Auric Chloride . .	$AuCl_3$	303·1	101	20·2	$\frac{N}{5}$
Platinic Chloride . .	$PtCl_4$	339·1	84·8	84·8	N
Magnesia Mixture (for Phosphoric Acid) .	—	—	—	— .	. N

Symbol of Substance taken.	Method of Preparing Reagent.
$CaSO_4,2Aq$	Water at 15·5° C. saturated with precipitated calcium sulphate.
$MgCl_2,6Aq$	101·5 grms. dissolved and diluted to 1 litre.
$MgSO_4,7Aq$	123 grms. " " "
$FeSO_4,7Aq$	139 " " "
—	18·67 grms. of iron, as $Fe_2H_6O_6$, dissolved in 200 cc. of 5 N hydrochloric acid and diluted to 1 litre.
$PbC_4H_6O_4,3Aq$	189·5 grms. dissolved and diluted to 1 litre.
PbN_2O_6	165·5 " " "
$AgNO_3$	170 " " "
"	34 " " "
Ag_2SO_4	Water at 15·5° C. saturated with freshly precipitated argentic sulphate.
$Hg_2N_2O_6,2Aq$	56 grms. dissolved in 40 cc. 5 N nitric acid and diluted to 1 litre, a little mercury being placed in bottle.
$HgCl_2$	54·2 grms. dissolved and diluted to 1 litre.
$CuSO_4,5Aq$	124·75 " " "
$CuCl_2,2Aq$	85·25 " " "
$SnCl_2,2Aq$	112·5 grms. dissolved in 200 cc. of 5 N hydrochloric acid and diluted to 1 litre, a little tin being placed in bottle.
—	13·1 grms. of metallic gold, converted into auric chloride, dissolved and diluted to 1 litre.
—	49·3 grms. of metallic platinum, converted into platinic chloride, dissolved and diluted to 1 litre.
—	Dissolve 68 grms. $MgCl_2,6Aq$ in about 500 cc. of water, add 165 grms. NH_4Cl, then 300 cc. of 5 N ammonium hydrate, and dilute to 1 litre.

QUESTIONS.

Group II.

1. What changes take place when the sulphides of As, Sb, and Sn are boiled, 1st, with $(NH_4)_2S$, 2nd, with NaHO? Express the changes by equations.
2. Give the formulæ of cinnabar, of white precipitate, and of mercuric nitrate.
3. Write out the symbolic equations for the reactions which mercuric chloride gives with the group and special reagents.
4. Calculate the percentage composition of white precipitate.
5. How is corrosive sublimate manufactured, and whence does it derive its name?
6. 1·5 grm. of $HgCl_2$ is precipitated as HgS and collected on a weighed filter. How much by weight of HgS should there be obtained?
7. Cinnabar is sometimes found adulterated with red-lead, red oxide of iron, brick-dust. State how you would discover the adulteration. (No separation of the impurities from each other is required.)
8. What reaction takes place when mercury is acted upon by concentrated sulphuric acid? and by what consecutive stages can the product of this reaction be converted into white precipitate?
9. How can Bi be separated from Ag, Pb, or Hg?
10. Express in symbolic equations the reactions which a bismuthous salt gives with different reagents in the wet way.
11. Give the formulæ for bismuthous nitrate, bismuthous oxide, bismuth glance, bismuthous oxychloride.
12. Calculate the percentage composition of an alloy of 1 atom of Pb, 1 atom of Sn, and 3 atoms of Bi.
13. How does copper occur in nature?
14. Express in symbolic equations the reactions of copper in the wet way.
15. Explain what takes place—
    1st, When copper is treated with concentrated HNO_3.
    2nd, " " " H_2SO_4.
    3rd, " " " HCl.
    Give equations.
16. How much metallic zinc is required to precipitate 1·5 grm. of copper from a cupric solution?
17. What is understood by nascent hydrogen?
18. What is the percentage of the metallic copper in malachite?
19. How is Cu separated from Ag, Pb, and Bi?
20. What change takes place when metallic copper is heated in air?
21. How much hydrogen gas (at 0° and 760 mm. pressure) is required to deprive 10 grms. of ignited cupric oxide of its oxygen, and how much water will be obtained?
22. Describe three methods of separation of Cd from Cu.
23. How is Cd separated from Pb, Ag, Bi, and Zn?
24. How much cadmium sulphide can be prepared from 10 grms. of crystallised cadmium sulphate, $CdSO_4$, $4OH_2$?
25. What takes place when greenockite is roasted in a glass tube open at both ends?

26. How is the metal cadmium converted 1st into oxide, 2nd into chloride, 3rd into sulphate?
27. How can we extract cadmium from its oxide or sulphide?
28. How do you detect a stannic salt in the presence of a stannous salt?
29. Give the formulæ of metastannic and stannic acids, stannous and stannic chlorides, and stannous oxychloride.
30. State the action of chlorine, nitric acid, and air upon stannous salts?
31. How would you analyse an alloy consisting of Pb, Cu, Bi, Sn?
32. A tinstone yielded on analysis 77·5 per cent. of metallic tin; how much SnO_2 did it contain?
33. How much chlorine gas by weight and by volume (at 0° and 760 mm.) will be absorbed by 10 grms. of $SnCl_2$?
34. How is antimonious chloride prepared? What change does it undergo when water is added to it?
35. By what characteristic reaction can antimony compounds be recognised by dry reactions?
36. How can you distinguish between antimonious and antimonic compounds?
37. What evidence have we to show the triad and pentad nature of Sb?
38. Give illustrations of the reducing action of antimonious compounds, *e.g.*, antimonious chloride.
39. State how you would separate Sb from Sn in solution.
40. How can Sn be separated from Bi?
41. 1 grm. of a sample of grey antimony yielded on analysis ·854 grm. of Sb_2O_4; what percentage of antimony does the ore contain?
42. How much chlorine by weight and by volume (at 0° C. and 760 mm.) is required to convert 10 grms. of $SbCl_3$ into $SbCl_5$?
43. How much oxygen gas by weight and by volume (at 0° C. and 760 mm.) can be obtained by igniting 5 grms. of Sb_2O_5?
44. *Which are the most important natural compounds of arsenic?*
45. Give the symbolic formulæ of realgar, orpiment, copper nickel, smaltine, nickel ochre.
46. What changes does metallic arsenic undergo when heated, 1st, by itself, in a current of neutral gas (CO_2 or H); 2ndly, in contact with air; 3rdly, in contact with chlorine?
47. What action has sulphuretted hydrogen upon an acid solution of arsenious and upon a solution of arsenic acid?
48. Express by an equation the reaction which takes place when arsenious sulphide is dissolved; 1st, in NaHO; 2ndly, in $(NH_4)_2S$; 3rdly, in NH_4HCO_3.
49. What precipitates are produced when silver nitrate is added to a neutral solution of an arsenite or arsenate?
50. What is the action of magnesium sulphate in an ammoniacal solution (so called magnesia mixture) upon arsenious and arsenic solutions?
51. Give a few instances of the reducing action of arsenious compounds. Express the changes by equations.
52. Explain the oxidising action of chlorine, bromine, and iodine upon arsenious compounds.
53. What takes place when metallic copper is introduced into a dilute hydrochloric acid solution: 1st, of As_2O_3; 2ndly, of As_2O_5 (Reinsch's test)?
54. Explain why a portion of the arsenic only is liberated, when an arsenical sulphide is heated with potassium cyanide. Give equations.
55. Explain the reduction of arsenical compounds by nascent hydrogen (Marsh's test), and show by equations the formation of arseniettted hydrogen.
56. What change does arseniettted hydrogen undergo: 1st, when burnt in the air; 2nd, when passed through a tube heated in one or more places; 3rd, when passed into a solution of silver nitrate; 4th, when passed through concentrated nitric acid?
57. Explain the formation of antimoniettted hydrogen, and state—1st, what properties arseniettted hydrogen has in common with antimoniettted hydrogen; and, 2nd, how it differs from the latter in its chemical deportment with silver nitrate.

58. How would you distinguish between an arsenic and antimony mirror?
59. Describe the cacodyl test—with equations.
60. How would you treat a silver coin containing a small quantity of gold in order to extract the latter metal from it?
61. How is $AuCl_3$ prepared?
62. Describe how pure metallic gold is prepared from $AuCl_3$ in the wet way.
63. Explain the change which Au_2S_3 undergoes, 1st, when gently heated in a bulb tube; 2nd, when heated in a tube open at both ends.
64. How can gold be separated from an alloy of Au, Ag, and Cu?
65. How is platinic chloride prepared? Give an equation.
66. How much Pt will be left, when 1·5 grm. of $2NH_4Cl,PtCl_4$ is ignited?
67. How is platinous chloride prepared?
68. How is silver nitrate prepared?
69. What change takes place when silver glance is roasted in a tube?
70. Write out the equations for the reactions of silver in the wet way.
71. How much NaCl will be required to convert 1·5 grm. of $AgNO_3$ into AgCl?
72. A dilute solution of hydrochloric acid (containing ·00365 grm. of the acid in one cubic centimetre of the solution) is precipitated with $AgNO_3$. How much AgCl by weight do we get from 150 cc. of the acid solution?
73. What is the percentage composition of silver acetate, and how much silver will be left when ·451 grm. of acetate is ignited?
74. What changes does AgCy undergo upon ignition?
75. How much oxygen by weight and by volume (at 0° C. and 760 mm.) can be obtained from 30 grms. of red lead?
76. Write out the symbolic equations for the reactions of lead in the wet way.
77. How can Pb be separated from Ag in the wet way?—1st, by using hydrochloric acid; 2nd, potassic cyanide; 3rd, sulphuric acid as a precipitant.
78. Describe how you would analyse an alloy of 5 parts of lead, 3 parts of tin, and 8 parts of bismuth, a so-called fusible alloy melting at 98° C.
79. Write out the formulæ of calomel, mercurous nitrate, mercurous oxide, mercurosoammonium chloride, basic dimercurosoammonium nitrate.
80. Write out equations for the reactions which mercurous compounds give in the wet way.
81. How can mercurous chloride be converted into mercuric chloride? Give equations.
82. How much calomel can be manufactured from 20 lbs. of metallic mercury; and how much H_2SO_4 and NaCl by weight will be required?
83. What is the action of boiling nitric acid upon mercurous sulphide?

Group IIIa.

1. Enumerate some of the most important iron ores used for the extraction of iron in this country.
2. Which are the more important sulphides of iron?
3. How is iron detected in the dry way?
4. What takes place when iron is dissolved in HCl, in H_2SO_4, or in dilute HNO_3?
5. Explain the change which takes place when $FeCl_2$ is severally acted upon by atmospheric air, by chlorine, $KClO_3$, and HCl, HNO_3, $HgCl_2$, $AuCl_3$, and by $Mn_2O_6(KO)_2$, and HCl. Express the changes by equations.
6. Explain the action of SH_2 and $(NH_4)_2S$ upon ferric salts, 1st, in acid solutions; 2nd, in neutral or alkaline solutions.
7. How do K_4FeCy_6 and $K_6Fe_2Cy_{12}$ enable us to distinguish between ferrous and ferric salts?
8. State why $K_6Fe_2Cy_{12}$, in the presence of $SnCl_2$ produces a blue precipitate with ferric salts.
9. State the action of SKCy upon ferrous and ferric salts.
10. What change is produced when Fe_2Cl_6 is brought together, 1st, with SO_2; 2nd, with $SnCl_2$?
11. Explain the action of metallic iron or metallic zinc upon $Fe_2(SO_4)_3$.

12. How much hydrogen gas by weight and volume (0° C. and 760 mm.) is obtained when 10 grms. of metallic iron is dissolved in dilute hydrochloric acid?
13. Describe the properties of ferric phosphate. State why an alkaline acetate has to be added previous to precipitation with hydrogen disodium phosphate, and explain the decomposition of the phosphates of the alkaline earths by means of ferric chloride in an acetic acid solution.
14. How much metallic iron is required to manufacture one ton of crystallised green vitriol?
15. How would you separate Fe_2O_3 from Zn″, Mn″, Ni″, Co″, and Fe″?
16. Why is it preferred to precipitate Fe_2Cl_6 by means of NH_4OH, instead of KHO?
17. What is the most important chromium ore?
18. How is chromium detected in the dry way?
19. Describe how chromic chloride or sulphate is obtained from an alkaline chromate.
20. Describe the reactions by double decomposition which you can produce with chromic salts. Give equations.
21. How can chromic salts be converted in the wet way into chromates? Give instances, and express the changes by equations.
22. How is chromic anhydride prepared?
23. Give instances of the oxidising action of chromic acid. Express the changes by symbolic equations.
24. You have given to you oxalic, hydrochloric, and concentrated sulphuric acids, potassium dichromate and water. State how you would prepare CO_2 and Cl gas from these materials, and express the changes by equations.
25. Describe some of the most characteristic reactions for chromic acid produced by double decomposition. Give equations.
26. How would you distinguish between a chromic salt and chromic acid occurring in one and the same solution?
27. Which chromates are soluble and which are insoluble in water?
28. How can Cr be separated from every other metal of Group III., except Mn?
29. How can Cr_2O_3 be separated from Fe″, Zn″, Mn″, Ni″, Co″ salts?
30. 1·600 grm. of chrome iron ore yielded on analysis 2·95 grms. of $PbCrO_4$. What percentage of Cr does the ore contain?
31. 1·2 grm. of a sample of a sodium chromate yielded with sulphuric and oxalic acids ·89 grm. of carbonic anhydride. What percentage of chromic anhydride did it contain?
32. Enumerate some of the more important aluminium minerals.
33. How is Al_2O_3 detected in the dry way?
34. Give equations for the reactions of aluminium in the wet way.
35. How can insoluble aluminium minerals be rendered soluble in water or acids?
36. What is the action of HF upon felspar and albite?
37. How can Al_2O_3 be separated from Fe_2O_3?
38. How is Al_2O_3 separated from Fe″, Zn″, Mn″, Ni″, Co″ in combination?
39. How can Al_2O_3 be distinguished from $Al_2P_2O_8$?

Group IIIb.

1. Express in symbolic equations the reactions for nickel in the wet way.
2. State which are the principal nickel minerals, and give the formulæ of nickel nitrate and arsenate.
3. Calculate the percentage composition of capillary pyrites.
4. Give the formulæ of cobalt pyrites, cobalt vitriol, cobalt bloom, cobaltic cyanide.
5. How is Co separated from Ni?
6. 2 grms. of an ore containing Ni and Co yield ·221 grm. of NiO and ·1575 grm. of Co_3O_4; what is the percentage of Ni and Co in the ore?
7. How would you prepare potassium cobalticyanide?

8. Which are the most important manganese ores?
9. Explain the action of concentrated H_2SO_4 upon MnO_2, Na_2MnO_4 and $K_2Mn_2O_8$; and express the changes by equations.
10. Describe the most characteristic blowpipe reactions for manganese compounds.
11. How can Mn be separated from Ni and Co?
12. How is Mn separated from calcium or from potassium?
13. What change does a solution of potassium manganate undergo when heated in contact with air?
14. State why Mn is separated with difficulty from Fe^{iv} by means of NH_4Cl and NH_4OH.
15. By precipitating 2·622 grms. of a manganous salt with sodium carbonate and ignition of the precipitate, 1·325 grm. of Mn_3O_4 is left; what is the percentage of manganese in the salt?
16. What is the action of potassium permanganate upon HCl, and upon acid solutions of SH_2, SO_2, oxalic acid, Cu_2Cl_2, $FeCl_2$, $SnCl_2$? Express the changes by equations.
17. How much sulphurous anhydride by weight and by volume (at 0° C. and 760 mm. barometrical pressure) will be required to decolorise a solution containing ·500 grm. of potassium permanganate?
18. ·125 grm. of potassium permanganate had to be added to a given quantity of an acid (H_2SO_4) solution of $FeSO_4$. Calculate how much metallic iron the solution contained.
19. 1240 grm. of CO_2 was evolved when 1·780 grm. of pyrolusite was treated with moderately concentrated H_2SO_4 and potassium oxalate. What is the percentage of MnO_2 in the ore, and how much chlorine gas by weight and by volume can be evolved from 100 grms. of the ore when treated with HCl?
20. State the action of HCl, H_2SO_4, HNO_3, and KHO upon metallic zinc. Express the changes by equations.
21. Give the names and composition of the most important zinc ores.
22. Describe the blowpipe reactions for zinc compounds.
23. Express by equations the reactions for zinc in solution.
24. 1·5 grm. of calamine yielded on analysis ·876 grm. of ZnO, what is the percentage of zinc in the ore?
25. You have given to you calamine, zinc blende, hydrochloric acid, water and sodium carbonate. State how you would prepare from these materials zinc oxide or zinc white. Express the changes by equations.
26. How is zinc separated from Mn, Ni, Co?

Group IV.

1. How can barium sulphate be converted into barium nitrate or chloride?
2. Express in symbolic equations the different reactions for barium.
3. Which are the most delicate reactions for barium?
4. How can barium be separated from strontium and calcium?
5. 1·235 grm. of witherite gave ·965 grm. of barium sulphate; what is the percentage of barium and of barium carbonate in the mineral?
6. How are strontium chloride and nitrate prepared—1st, from strontianite; 2nd, from celestine?
7. Which are the most characteristic reactions for strontium?
8. How can strontium be distinguished from barium?
9. How can strontium be separated from calcium?
10. Which are the most important natural lime compounds?
11. Which are the most delicate reactions for calcium in the wet way?
12. Calculate the percentage composition of bone ash.

Groups V. & VI.

1. How are potassium compounds recognised in the wet way?
2. How can potassium and sodium compounds be distinguished before the blowpipe flame?

3. State how you would ascertain whether the yellow precipitate produced by platinic chloride indicates the presence of a salt of ammonium or potassium, or both?
4. How can hydrogen potassium tartrate be distinguished from hydrogen ammonium tartrate?
5. Which sodium salts are found native?
6. How is spongy platinum prepared?
7. How would you test for mere traces of ammonia?
8. How much spongy platinum is obtained from 2·345 grms. of ammonium platinic chloride?
9. How much dry ammonia gas by volume (litres) and weight can be obtained by distillation with calcium hydrate from 5 grms. of ammonium chloride?
10. How would you examine a mixture containing ammonium chloride and potassium chloride?
11. A mixture of 1·5 grm. of sodium and ammonium chlorides lost on ignition ·234 grm.; what is the percentage of ammonium and sodium chloride present in the mixture?
12. Calculate the percentage composition of borax.
13. Give examples of the action of different salts on ammonium compounds.
14. How is magnesium sulphate prepared—1st, from magnesite; 2nd, from dolomite?
15. Which are the most important magnesium minerals?
16. Explain the action which ammonia, potassium hydrate, and sodium carbonate have upon solutions of magnesium salts in the presence of ammonium salts, and also without them?
17. Describe fully the most characteristic reaction for magnesium salts in the wet way.
18. How is magnesium separated from potassium and sodium?
19. How much crystallised magnesium sulphate, $MgSO_4,7OH_2$, can be prepared from one ton of pure magnesite?

Carbonic Acid.

1. How would you prove experimentally the presence of carbonic anhydride—1st, in spring water; 2nd, in atmospheric air; 3rd, in white lead; 4th, in coal gas?
2. Classify all metallic carbonates according to their respective deportment—1st, on ignition; 2nd, on treatment with water; 3rd, in contact with excess of CO_2. Give examples.
3. What change takes place when tartaric acid and hydrogen potassium carbonate are mixed together?
4. Which is the most characteristic reaction for CO_2?
5. How would you recognise the presence of CO_2 in a gaseous mixture, containing SO_2 and CO_2, or SH_2 and CO_2?
6. How much CO_2, by weight and by volume, can be obtained from 1·235 grm. of $CaCO_3$?
7. What change takes place—1st, when a current of CO_2 is passed through cold water in which finely divided chalk is suspended; and 2nd, when the liquid is heated to boiling, subsequent to the passing of the gas?
8. Explain the effect of boiling upon most spring waters.
9. What is the usual composition of boiler deposits, and how would you propose to prevent them?

Sulphuric Acid.

1. Classify all metallic sulphates according to their solubility in water.
2. How are metallic sulphates detected in the dry way?
3. Explain the action of heat upon the different metallic sulphates.
4. How is free sulphuric acid detected?

5. Describe shortly in what manner sulphates of Ba, Sr, Ca, Mg, and Pb differ from each other with regard to their solubility in water, and their respective deportment with various other solvents.
6. How are insoluble sulphates examined qualitatively?

Sulphurous Acid.

1. Describe different methods of preparing sulphurous anhydride.
2. What is the action of heat upon sulphides?
3. Which sulphites are soluble and which are insoluble in water?
4. Give illustrations of the reducing action of sulphurous acid or of soluble sulphites.
5. Explain under what circumstances sulphuric acid can act as an oxidising agent; give instances of such action.
6. How would you distinguish sulphurous in the presence of sulphuric acid?
7. What changes take place when a mixture of potassium dichromate and sodium sulphite is treated with concentrated HCl? Give equations

Thiosulphates.

1. How is sodium thiosulphate prepared?
2. How are hyposulphites affected by ignition?
3. Explain the action of sodium hyposulphite upon lead, silver, mercurous, and stannous salts.
4. Give instances—1st, of the reducing action, and 2nd, of the oxidising action of hyposulphites.
5. State what application sodium hyposulphite has found in photography and in metallurgy.
6. How would you separate barium hyposulphite from barium sulphate?

Sulphides.

1. Which sulphides are soluble and which are insoluble in water?
2. Explain how certain sulphides are affected by dilute hydrochloric acid, and how by concentrated hydrochloric acid. Give characteristic instances, and express the changes by equations.
3. Describe the most delicate reaction for gaseous SH_2.
4. What is the action of nitric acid upon ZnS, PbS, CuS, SnS, Sb_2S_3?
5. How would you prove the presence of an alkaline sulphide, thiosulphate, sulphite, and sulphate in an aqueous solution?
6. How can you prove the presence of SH_2 in coal gas?
7. 10 litres of unpurified coal gas yielded ·232 grm. of CdS. What is the percentage of SH_2 in the gas?
8. What change takes place when PtS_2, Sb_2S_5, FeS_2, As_2S_3, and HgS are heated with exclusion of air?
9. How would you detect sulphur in pig iron?
10. Explain the action of chlorine, bromine, and iodine upon SH_2.

Nitrates.

1. Explain what changes take place when nitrates are heated by themselves.
2. State what action takes place when ferrous chloride is heated with nitric acid.
3. Why can the metals Cu, Pb, Ag, be employed for the detection of nitric acid or a nitrate?
4. How can ammonia be obtained from a nitrate? Describe several processes.
5. How is free nitric acid detected in the presence of a nitrate?

1. Explain the changes which take place when N_2O_4 is acted upon by KHO.
2. What is the action of dilute sulphuric acid upon KNO_2?

3. What are the products of decomposition of strongly ignited $Pb(NO_3)_2$, NH_4NO_3, and KNO_3?
4. How can a trace of a nitrite be detected in the presence of a nitrate?
5. Explain the action of heat upon a solution of $Ca(NO_2)_2$ and NH_4Cl.

Chlorides.

1. How are the several solid chlorides acted upon by heat?
2. How is chlorochromic acid prepared?
3. Classify all chlorides according to their solubility in water.
4. Describe the most characteristic tests for chlorine, as well as for hydrochloric acid or chlorides.
5. How would you detect free HCl in the presence of a metallic chloride?
6. You have given to you 100 cc. of a liquid containing free HCl and a solution of sodium chloride, 50 cc. of the liquid gave 2·345 grms. of AgCl. After evaporation and ignition of the other 50 cc. the residue yielded on precipitation with silver nitrate 1·596 grm. of AgCl. What is the percentage of HCl and of sodium chloride in the liquid?

Chlorates.

1. State briefly how potassium chlorate is prepared.
2. Describe the changes which potassium chlorate undergoes on ignition.
3. Explain the action 1st, of concentrated sulphuric acid; 2nd, of concentrated hydrochloric acid upon potassium chlorate. Give equations.
4. How can a chlorate be detected in the presence of a chloride?
5. How can a nitrate and a chloride be recognised in the presence of a chlorate?

Hypochlorites.

1. Give the formula for calcium chlorohypochlorite.
2. Give illustrations of the oxidising action of hypochlorites. Express the changes by equations.
3. How is bleaching powder prepared?
4. What change takes place—1st, when hypochlorite is ignited by itself; 2nd, when a concentrated solution of a hypochlorite is boiled?
5. How can a hypochlorite be distinguished in the presence of a chloride?

Bromides.

1. Describe a method by which bromine can be obtained from a soluble bromide.
2. Classify all bromides according to their solubility in water.
3. Describe the most characteristic tests for bromine, and for HBr.
4. Explain the action of chlorine, dilute HCl, concentrated H_2SO_4, concentrated HNO_3, and of H_3PO_4, upon potassium bromide.
5. How is HBr distinguished from HCl?
6. What takes place when bromine, phosphorus, and water are brought together?
7. Explain the action of SH_2, Na_2SO_3, and $Na_2S_2O_3$, upon bromine suspended in water.
8. Give the molecular weights of bromine and of hydrobromic acid.

Iodides.

1. How would you extract iodine from MgI_2? Give several methods, and express the changes by equations.
2. Explain the action of heat upon solid iodides.
3. Classify all iodides according to their solubility in water.
4. Explain how you would distinguish HCl, HBr, and HI, when occurring in one and the same substance.

5. Why is it preferable to liberate iodine by means of N_2O_3, instead of by bromine or chlorine?
6. How would you prepare a solution of hydriodic acid?
7. Explain how you would distinguish free iodine in the presence of an iodide.
8. What action takes place when a dilute solution of SO_2 acts upon iodine, and how can iodine be made the measure for SO_2 and *vice versâ*?
9. 10 litres of a mineral water yield ·134 grm. of AgI; how much iodine is there in 100,000 parts of the water?

Fluorides.

1. Which are the most important natural compounds of fluorine?
2. What changes do solid fluorides undergo when heated by themselves; 2ndly, when mixed with microcosmic salt or hydrogen potassium sulphate?
3. Classify fluorides according to their solubility in water.
4. How is hydrofluoric gas prepared? Explain its action upon glass.
5. How would you test for small quantities of a fluoride?
6. Explain the action of concentrated sulphuric acid upon a fluoride containing much SiO_2.
7. How can fluorine be detected in a mineral containing a silicate which is not decomposed by sulphuric acid, some phosphate, and traces of a fluoride?
8. How is $2HF,SiF_4$ prepared?
9. What decomposition takes place when silicofluorides are heated—1st, by themselves; 2ndly, with concentrated H_2SO_4?
10. How is BaF_2,SiF_4 obtained?

Phosphates.

1. How does phosphoric acid occur in nature?
2. Explain the action of heat upon H_2NaPO_4, NH_4MgPO_4, and $HNaNH_4PO_4$.
3. How are meta- and pyro-phosphates converted into tribasic phosphates?
4. Classify all phosphates, pyrophosphates, phosphites, and hypophosphites according to their solubility in water.
5. How is phosphoric acid removed from alkaline earthy phosphates?
6. State how you would detect phosphoric acid in a soil or iron ore; or phosphorus in metallic copper or cast iron.
7. What is the approximate composition of ammonium phospho-molybdate?
8. What reactions enable us to distinguish between tribasic, tetrabasic, and monobasic phosphates?
9. How would you prepare HH_2PO_2 and $Ca(H_2PO_2)_2$?
10. How are calcium phosphite and potassium hypophosphite acted upon by heat?
11. What are the products of oxidation obtained on burning PH_3 in air?
12. How can potassium hypophosphite be detected in the presence of potassium phosphite and phosphate?
13. How would you prepare gaseous PH_3? What is its action upon solutions of cupric sulphate and silver nitrate?
14. Give symbolic formulæ for gaseous phosphoretted hydrogen, calcium hypophosphite, cupric phosphide.
15. Express by a symbolic equation the change which HH_2PO_2 undergoes when it is acted upon by H_2SO_4, by $CuSO_4$, or by $AuCl_3$.
16. How would you convert bone-ash into a soluble calcium phosphate (into $H_4CaP_2O_8$—a constituent of calcium superphosphate)?
17. 5·4 grms. of cast iron yielded ·046 of $Mg_2P_2O_7$; what is the percentage of phosphorus in the iron?

Silicates.

1. Give instances of crystalline and amorphous silica.
2. Describe the reactions for SiO_2 in the dry way.

3. Classify silicates according to their solubility in water and acids.
4. Explain the action of HF, or of CaF_2, and concentrated H_2SO_4 upon silicates.
5. How would you ascertain the presence of potassium or sodium in a silicate soluble in HCl, and in a silicate, insoluble in HCl, *e.g.*, in Bohemian glass?
6. What is the action of caustic and carbonated alkalies upon amorphous silica?

Borates.

1. How is metaboric acid obtained?
2. Explain the reactions in the dry way for boric acid or borates.
3. Classify borates according to their solubility in water.
4. Explain the colour test for boric acid.
5. Explain the action of HF upon boric acid.

Cyanogen Compounds.

1. How are KCy and K_4FeCy_6 prepared?
2. Explain the action of heat upon KCy and K_4FeCy_6—1st out of contact with air; 2nd, with free access of air.
3. What constitutes the usefulness of KCy as a reagent for blowpipe experiments?
4. Explain the changes which cyanides of the heavy metals undergo upon ignition.
5. How would you prepare cyanogen gas? Describe its properties.
6. Classify cyanides according to their solubility in water. Enumerate some of the more important single cyanides.
7. Explain the action of dilute acids upon single cyanides and upon easily decomposable double cyanides.
8. Explain the action of SH_2 upon the following cyanides and double cyanides: $HgCy_2$, K_2CdCy_4, $KAgCy_2$, K_4MnCy_6, K_2CuCy_4, K_2CoCy_4, K_2NiCy_4.
9. How is AgCy distinguished from AgCl?
10. Describe the action of HCy upon $S(NH_4)_2$, and explain how traces of HCy can be detected in the presence of ferro- or ferri-cyanogen compounds.
11. Explain the use of ferro-ferric salts for the detection of HCy.
12. How is HCy prepared? Describe its properties.
13. How could you examine a ferrocyanide insoluble in acids, *e.g.*, Prussian blue?
14. State the action of KHO upon Prussian blue and upon Turnbull's blue.
15. State what reactions ferrous and ferric salts give with ferro- and ferri-cyanides.
16. Explain the formation of soluble Prussian blue.
17. What is the action of dilute and of concentrated sulphuric acid upon potassium ferrocyanide?
18. Explain the conversion of potassium ferro- into ferri-cyanide.
19. Give instances of the oxidising action of potassium ferricyanide in alkaline solutions.
20. How can silver ferro- and ferri-cyanides be separated from each other?
21. How is OHCy recognised in the presence of a cyanide?
22. What is the action of concentrated H_2SO_4 upon a cyanate?
23. Explain the formation of potassium sulphocyanate, and state what change it undergoes when heated in contact with air.
24. Why does potassium sulphocyanate enable us to distinguish between ferrous and ferric salts?
25. Calculate the percentage composition of cuprous sulphocyanate, $Cu_2(SCy)_2$.

Carbonylic Acids.

1. What elements enter into the composition of organic acids?
2. How are the several salts of organic acids influenced by heat, and what inference can be drawn from this action?

3. How is formic acid obtained, and what changes do formates undergo when heated out of contact with air?
4. How can a formate be detected in solution?
5. State how acetic acid is prepared.
6. What is the action of heat upon dry acetates?
7. How would you prepare marsh-gas?
8. Explain the action of acetic acid upon silver carbonate or lead oxide.
9. What residue is left on igniting sodium acetate, calcium acetate, lead acetate, or silver acetate?
10. Explain how you would obtain acetic ether, describe its composition and properties.
11. A quantity of crystallised silver acetate leaves upon ignition 1·236 grm. of metallic silver. How much acetic acid does this correspond to?
12. How much dry sodium acetate must there be decomposed in order to obtain 20 litres of marsh-gas?
13. How are benzoic and succinic acids prepared?
14. State how the precipitate produced by $\overline{Bz}HO$ and $\overline{Su}HO_2$ with Fe_2Cl_6 assists in distinguishing between these two acids.
15. How would you prepare benzene from benzoic acid?
16. 1·340 grm. of the silver salt of an organic acid leaves upon ignition ·632 grm. of metallic Ag. What is the molecular weight of the acid?
17. How is oxalic acid obtained? Describe shortly its properties.
18. What changes does oxalic acid undergo—1st, upon ignition; 2nd, upon heating with H_2SO_4; 3rd, upon treatment with H_2SO_4 and MnO_2 or $K_2Cr_2O_7$; 4th, in contact with $AuCl_3$?
19. How would you distinguish calcium oxalate from calcium carbonate, fluoride, borate, or phosphate?
20. What takes place when potassium, silver, calcium, or zinc oxalate is ignited by itself?
21. How would you prepare pure carbonic oxide gas from sodium oxalate?
22. The calcium salts in one litre of water are precipitated with ammonium oxalate. The precipitate yields upon ignition 1·695 grm. of $CaCO_3$. How much CaO does the water contain—1st, per gallon; 2nd, per 100,000 parts?
23. Describe some sources of tartaric acid.
24. Describe the decomposition which tartaric acid and tartrates undergo upon ignition.
25. How can tartaric acid be detected in solutions?
26. Whence is citric acid derived?
27. Describe the tests which distinguish citric from tartaric acid.
28. How would you detect oxalic, tartaric, and citric acids contained in a liquid?
29. Why does the presence of citric or tartaric acid prevent the precipitation of Al_2O_3 or Fe_2O_3 by NH_4OH?

SUMMARISED TABLE OF DRY REACTIONS FOR METALS.

SUMMARISED TABLE OF
OPERA

Analytical Group.	Metal.	Compound Heated in Dry Tube.	Moistened with HCl and Heated on Platinum Wire.	Heated in Borax Bead in Blowpipe Flame.	
		Residue is :	*Flame is coloured :*	*Outer flame.*	*Inner flame.*
I.	Pb	Red, hot; yellow, cold; fusible.	Bluish.	Nothing marked.	
	Ag	Brownish, hot; metallic, cold.	—	,,	,,
	Hg	Sublimate of metal.*		,,	,,
II. *a*	Bi	Yellow, cold; infusible.	Bluish.	—	
	Cu	Black, hot and cold, infusible.	Green.	Light blue.	Red.
	Cd	Brown, hot; lighter, cold, infusible.*	—	Nothing marked.	
II. *β*	As	Sublimate.*	Pale blue, thin.	,,	,,
	Sb	,,	,, denser.	,,	,,
	Sn	Yellow, hot; paler, cold, infusible.	,, streaky.	,,	,,
III. *a*	Fe	Dark red.	—	Red, hot; yellow, cold.	Pale green.
	Al	White.	—	—	
	Cr	Green or purple.	—	Green.	Green.
III. *β*	Mn	Black or dark red.	Greenish yellow.	Amethyst.	Colourless.
	Zn	White.	Thin, streaky green.	—	
	Ni	Black.	—	Violet or reddish.	Greyish.
	Co	,,	—	Deep blue (sapphire).	Deep blue.
IV.	Ba	White.	Yellow-green.	—	
	Sr	,,	Crimson-red.	—	
	Ca	,,	Pale-red.		
V. *a*	Mg	White.	—		
	K	,, fusible.§	Violet.		
	Na	,, ,, §	Yellow.		
V. *β*	NH_4	Sublimate.	—		

RY REACTIONS FOR METALS.

ONS.

Heated on Charcoal.‡ *Metallic bead*	and *Incrustation.*	Heated with Na_2CO_3 on Charcoal.‡ *Bead or Residue.*	Fused on platinum foil with Na_2CO_3 and KNO_3.
hite, soft.	Yellow.	White, soft, marks paper.	—
White.	None.	White, malleable.	—
. .	. .	. . . .	. . .
White, brittle.	Yellow.	White, brittle, very fusible.	—
ed scales.	—	Red, malleable.	—
ard to get.	Brown.	White, soft, very fusible.	—
Strong odour.	White.	Strong odour.	—
White fumes.	Bluish white.	White, brittle.	—
uminous.†	—	—	—
Black metallic residue, agnetic.	None.	Black metallic particles, magnetic.	—
White uminous esidue.†	,,	White residue.	—
Green.	,,	Green or yellow mass.	Yellow mass $= K_2CrO_4$.
Black.	,,	Black residue.	Blue-green enamel.
White uminous esidue.†	White.	White ,,	—
Black agnetic esidue.	None.	Black magnetic residue.	—
Black agnetic esidue.	,,	Black magnetic residue.	—
White minous.†	,,	Same, less distinct.	—
White minous.†	,,		—
White minous.†	,,		—
White minous.†	,,	—	—
inks into charcoal.		—	—
,, ,,	,,	—	—
White fumes.		—	—

Remarks and Notes.

I.

* Sublimate is treated with SH_2 by passing the gas into tube.
Hg becomes black.
Cd } light yellow.
As } ,,
Sb ,, orange.
NH_4 unchanged.

II.

Heated in tube with black flux,
Hg gives globules of metal;
Sb and As give black ring and mirror in tube;
Cd gives brown ring and bright mirror.

† White luminous infusible residues *only* are to be moistened with CoN_2O_6 solution and again heated, when
Al becomes blue.
Zn ,, green.
Mg ,, pink.
Sn ,, dirty green.
Earthy phosphates and all borates become purple or blue.

‡ The appearances are very similar. If an incrustation is given on charcoal alone it is also given when Na_2CO_3 is used.

§ If the acid be *olourless.*

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